

PATENT ABSTRACTS OF JAPAN

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(54) MULTILAYER PRINTED WIRING BOARD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a printed wiring board with which a through-hole and a via hole are assured of connection reliability in restraining a filler from shrinking on curing.

SOLUTION: Interlayer resin insulating layers and conductor layers are alternately laminated on a board provided with a conductor layer, and inner and outer conductor layers are mutually connected through via holes to form a build-up wiring layer for the formation of a multilayer printed wiring board, wherein a through-hole is provided to the board to electrically connect the front and rear of the boards together, a non-conductive filler which contains metal particles is filled into the through-hole, and a conductor layer is formed on the exposed surface of the filler in the through-hole. It is preferable that the filler be composed of metal particles, resin, and inorganic fine powder and has 1 MΩ.cm or above in resistivity.

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CLAIMS

[Claim(s)]

[Claim 1] In the multilayer printed wiring board with which the build up wiring layer which carried out the laminating of the resin insulating layer between layers and the conductor layer by turns, and connected the conductor layers of an inside-and-outside layer in the Bahia hall is formed on the substrate which has a conductor layer The multilayer printed wiring board characterized by forming the through hole which connects a front face and a rear face to said substrate electrically, filling up the through hole with the non-conductive filler containing metal particles, and forming the wrap conductor layer in the exposure from the through hole of the filler further.

[Claim 2] The multilayer printed wiring board according to claim 1 characterized by connecting the filler to the wrap aforementioned conductor layer in the Bahia hall.

[Claim 3] Said filler is a multilayer printed wiring board according to claim 1 or 2 characterized by consisting of metal particles, resin, and the end of inorganic superfines.

[Claim 4] Said filler is a multilayer printed wiring board given in any 1 of claims 1-3 characterized by specific resistance being 1 or more M omega-cm.

[Claim 5] Mean particle diameter said metal particles Multilayer printed wiring board given in any 1 of claims 1-4 characterized by being 0.1-30 micrometers.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention is proposed about a multilayer printed wiring board about the multilayer printed wiring board which controlled hardening contraction of a filler and secured the connection dependability of a through hole and the Bahia hall.

[0002]

[Description of the Prior Art] In recent years, the package substrate which mounts IC chip corresponds to the miniaturization or improvement in the speed of electronic equipment accompanying the advance of electronic industry, and the densification by the fine pattern and what has high dependability are called for.

[0003] As such a package substrate, a plating through hole is filled up with conductive paste, and the thing in which the conductor layer which covers this conductive paste was formed is indicated by JP,5-243728,A.

[0004]

[Problem(s) to be Solved by the Invention] However, in the package substrate concerning the conventional technique of upper **, since conductive paste was used, hardening contraction of the resin needed to be carried out and conductivity needed to be produced. For this reason, in this package substrate, when it was easy to produce the clearance resulting from hardening contraction of a filler between conductive paste and the conductor of a through hole wall and it put to the bottom of an elevated temperature and a humid condition, the problem that the conductor layer which covers conductive paste exfoliated, or an open circuit occurred a through hole, the Bahia hall, and in between arose.

[0005] Then, this invention aims at offering the printed wired board which controlled hardening contraction of a filler and secured the connection dependability of a through hole and the Bahia hall.

[0006]

[Means for Solving the Problem] Artificers hit on an idea of the following contents to invention considered as a summary configuration, as a result of inquiring wholeheartedly towards implementation of the above-mentioned purpose.

(1) The multilayer printed wiring board of this invention on the substrate which has a conductor layer In the multilayer printed wiring board with which the build up wiring layer which carried out the laminating of the resin insulating layer between layers and the conductor layer by turns, and connected the conductor layers of an inside-and-outside layer in the Bahia hall is formed to said substrate The through hole which connects a front face and a rear face electrically is formed, the through hole is filled up with the non-conductive filler containing metal particles, and it is characterized by forming the wrap conductor layer in the exposure from the through hole of the filler further.

[0007] In addition, in the above-mentioned multilayer printed wiring board, it is desirable that the filler is connected to the wrap aforementioned conductor layer in the Bahia hall, and, as for said filler, it is desirable that metal particles, resin, and mean particle diameter consist of the inorganic superfines end of 1-1000nm preferably. Moreover, for said filler, specific resistance is

1x108 more desirably 1 or more M omega-cm. It is more than omega-cm and the mean particle diameter said metal particles It is desirable that it is 0.1–30 micrometers.
[0008]

[Embodiment of the Invention] the hardening contraction for giving conductivity to the filler containing metal particles, since a filler and its filler are excelled in adhesion with a wrap conductor layer since the filler which contains metal particles as an ingredient which fills a through hole is being used for the multilayer printed wiring board of such this invention, and the non-conductive filler is used -- it is not necessary to give -- a through hole wall -- exfoliation of the filler from a conductor can be prevented. It is because a conductor layer is pushed up and is made to exfoliate under heat-and-high-humidity conditions if such exfoliation exists, in case water collects and this water volatilizes.

[0009] It is desirable to use the constituent as for which metal particles, resin, and mean particle diameter become especially desirable as a filler from the inorganic superfines end of 1–1000nm (preferably 2–100nm) in this invention. The network structure in which this reason is formed of the intermolecular force after inorganic superfines carries out the trap of the metal particles, and those metal particles do not sediment. For this reason, it is because the conductor layer with which metal particles cover a projection, and this metal particles and it can unite with a filler front face and that adhesion can be raised. Exfoliation with a filler and a through hole conductor layer is prevented, and exfoliation with the conductor layer which covers a filler and this filler also with the bottom of heat-and-high-humidity conditions stops thereby, occurring.

[0010] Here, as metal particles which constitute said filler, copper, gold, silver, aluminum, nickel, titanium, chromium, tin/lead, palladium, etc. can be used. These metal particles may give metal surface treatment agents, such as a complexing agent, etc. to that front face, in order to improve adhesion with resin. That mean particle diameter these metal particles It is desirable that it is 0.1–30 micrometers. This reason is that it is the range which can secure adhesion with the conductor layer which covers a filler. Moreover, as for the loadings of these metal particles, it is desirable to consider as 30 – 90 % of the weight to the total solids of a filler. This reason is that it is the range which can secure adhesion and printing nature to coincidence.

[0011] Moreover, thermosetting resin and thermoplastics can be used as matrix resin which constitutes said filler. As thermosetting resin, any or at least one sort of resin chosen from an epoxy resin, polyimide resin, and phenol resin is good. As thermoplastics, polytetrafluoroethylene (PTFE), Fluororesins, such as an ethylene tetrafluoride 6 fluoride propylene copolymer (FEP) and an ethylene tetrafluoride perphloro alkoxy copolymer (PFA), Polyethylene terephthalate (PET), polysulfone (PSF), A polyphenylene sulfide (PPS), thermoplastic mold polyphenylene ether (PPE), Any which are chosen from polyether sulfone (PES), polyether imide (PEI), polyphenylene sulfone (PPES), polyethylenenaphthalate (PEN), a polyether ether ketone (PEEK), and polyolefine system resin or at least one sort is good.

[0012] it is chosen out of a bisphenol mold epoxy resin and a novolak mold epoxy resin as optimal resin especially used for a filler -- one sort is good even if few either. When a bisphenol mold epoxy resin chooses resin, such as A mold and a female mold, suitably, even if a diluent solvent is not used for this reason, that viscosity can be adjusted, and a novolak mold epoxy resin is excellent in thermal resistance or chemical resistance with high intensity, and is not disassembled in a strong base nature solution like nonelectrolytic plating liquid, and it is because it does not pyrolyze. As said bisphenol mold epoxy resin, even if few either, the thing which is chosen from the bisphenol A mold epoxy resin and a bisphenol female mold epoxy resin and which use one sort is desirable. Especially, since a bisphenol female mold epoxy resin can be used with a non-solvent by hypoviscosity, it is advantageous. As said novolak mold epoxy resin, even if few either, the thing which is chosen from a phenol novolak mold epoxy resin and a cresol novolak mold epoxy resin and which use one sort is desirable. When blending and using a novolak mold epoxy resin and a bisphenol mold epoxy resin in such resin, the blending ratio of coal is 1 / 1 – 1/100 at a weight ratio. It is desirable. This reason is because it is the range which can prevent sedimentation of metal particles, controlling the rise of viscosity.

[0013] As an inorganic ultrafine particle which constitutes said filler, it is desirable to use a silica, an alumina, silicon carbide, and a mullite. A silica is the optimal especially. The mean particle

diameter of this inorganic ultrafine particle is 2–100nm more preferably 1–1000nm. It carries out. This reason is that it is the range which can form association presumed to be hydrogen bond in the shape of a mesh, and can carry out the trap of the particulate matter, without spoiling the restoration nature of a through hole, since particle diameter is detailed. These loadings after inorganic superfines receive the total solids of a filler. It is desirable to consider as 0.1 – 5 % of the weight. This reason is that it is the range which can prevent hardening contraction, without spoiling restoration nature.

[0014] In addition, as a curing agent used for such a resin constituent, an imidazole system curing agent, an acid-anhydride curing agent, and an amine system curing agent are desirable. It is because hardening contraction is small. By controlling hardening contraction, it can really [of a filler and the conductor layer which covers it] turn, and the adhesion can be raised.

[0015] Moreover, the resin constituent before such hardening can be diluted with a solvent if needed. As this solvent, there are the cyclohexanol of NMP (normal methyl pyrrolidone), DMDG (diethylene-glycol wood ether), a glycerol, water, 1-, 2-, or 3-, a cyclohexanone, methyl Cellosolve, methyl Cellosolve acetate, a methanol, ethanol, a butanol, propanol, etc.

[0016] At this invention, it is the specific resistance of a filler 106 It is 108 more preferably more than omega-cm. It carries out to more than omega-cm, and considers as non-conductive. the time of grinding, after hardening that resin constituent if this reason makes a filler conductivity – – polish waste — a conductor — it is because it adheres between circuits and becomes a short cause. Moreover, although it is necessary to make it carry out hardening contraction that the above-mentioned resin constituent gives conductivity, it is because carrying out hardening contraction will cause exfoliation with the conductor layer which covers a filler, so it is not desirable.

[0017] In this invention, the through hole and the filler may be connected in the Bahia hall on the wrap conductor layer. This reason is that it can lose the dead space by the through hole.

[0018] In order to make a wiring consistency high in this invention, it is desirable to form the conductor layer in the inner layer of a substrate. At this time, a substrate carries out the laminating of the prepreg to a conductor layer by turns, and it comes to form it. For example, a substrate carries out the laminating of the prepreg which resin was infiltrated into the cloth or nonwoven fabric of a glass fiber or an aramid fiber, and was made into B stage to copper foil or the circuit board by turns, and is formed by carrying out hot press and unifying.

[0019] the wall of the through hole where a filler is filled up with this invention — a conductor — it is desirable to form the roughening layer in a front face. This reason is that a filler and a through hole stick through a roughening layer, and a clearance does not occur. If an opening exists between a filler and a through hole, the conductor layer formed in right above [of it] with electrolysis plating will not become flat, or the air in an opening carries out thermal expansion of it, and it causes a crack and exfoliation, and is one side, and an opening is covered with water and it causes migration and a crack. If this point and a roughening layer are formed, such defect generating can be prevented.

[0020] moreover, this invention — setting — a filler — the front face of a wrap conductor layer — the conductor of a through hole wall — it is advantageous that the roughening layer formed in the front face and the same roughening layer are formed. This reason is that adhesion with the resin insulating layer between layers or the Bahia hall is improvable with a roughening layer. If the roughening layer is especially formed in the side face of a conductor layer, the crack generated towards the resin insulating layer between layers with these interfaces as the starting point with the lack of adhesion of a conductor-layer side face and the resin insulating layer between layers can be controlled.

[0021] The thickness of the roughening layer formed in the front face of such a through hole wall or a conductor layer has good 0.1–10 micrometers. This reason is that it will become a short cause between layers if too thick, and the adhesion force with adherend will become low if too thin. What carried out oxidation (melanism)-reduction processing and formed the conductor of a through hole wall or the front face of a conductor layer as this roughening layer, the thing processed and formed with the mixed water solution of an organic acid and the second copper complex, or the thing formed by plating processing of a copper-nickel-Lynn needlelike alloy is

good.

[0022] Let an oxidation bath (melanism bath), NaOH (2.7 g/l), and NaBH₄ (1.0 g/l.) be reduction baths for NaOH (20 g/l), NaClO₂ (50 g/l), and Na₃PO₄ (15.0 g/l) by the approach by oxidation (melanism)-reduction processing among these processings.

[0023] moreover — the processing using the water solution of the organic-acid-second copper complex — the bottom of oxygen coexistence conditions, such as a spray and bubbling, — as follows — acting — a conductor — metallic foils, such as copper which is a circuit, are dissolved.

$\text{Cu} + \text{Cu(II)} \text{ An} \rightarrow 2\text{Cu(I)} \text{ An}/2 \quad 2\text{Cu(I)} \text{ An}/2 + \text{n}/4\text{O}_2 + \text{nAH (aeration)}$

$\rightarrow 2\text{Cu(II)} \text{ An} + \text{n}/2\text{H}_2$ OA is complexing agents (it acts as a chelating agent), and n is the coordination number.

[0024] The second copper complex used by this processing has the good second copper complex of azoles. The second copper complex of these azoles acts as an oxidizer for oxidizing metal copper etc. As azoles, diazole, triazole, and tetrazole are good. An imidazole, 2-methylimidazole, 2-ethyl imidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 2-undecylimidazole, etc. are good especially. The content of the second copper complex of these azoles has 1 – 15 good % of the weight. It is because it excels in solubility and stability if it is within the limits of this.

[0025] Moreover, an organic acid is combined in order to dissolve copper oxide. As an example, any which are chosen from a formic acid, an acetic acid, a propionic acid, butanoic acid, a valeric acid, a caproic acid, an acrylic acid, a crotonic acid, oxalic acid, a malonic acid, a succinic acid, a glutaric acid, a maleic acid, a benzoic acid, a glycolic acid, a lactic acid, a malic acid, and sulfamic acid or at least one sort is good. The content of this organic acid and 0.1 – 30 % of the weight are good. It is for maintaining the solubility of oxidized copper and securing dissolution stability. In addition, the generated first copper complex dissolves in an operation of an acid, it combines with oxygen, and it turns into the second copper complex, and is again contributed to copper oxidation. Moreover, in addition to an organic acid, inorganic acids, such as a HOUFUTSU acid, a hydrochloric acid, and a sulfuric acid, may be added.

[0026] In order to assist the dissolution of copper and the oxidation of azoles, halogen ion, for example, fluorine ion, a chlorine ion, bromine ion, etc. may be added to the etching reagent which consists of this organic-acid-second copper complex. This halogen ion can add and supply a hydrochloric acid, a sodium chloride, etc. The amount of halogen ion has 0.01 – 20 good % of the weight. It is because the formed roughening layer is excellent in adhesion with the resin insulating layer between layers if it is within the limits of this.

[0027] The etching reagent which consists of this organic-acid-second copper complex dissolves in water, and prepares the second copper complex and organic acid (the need is accepted and it is the halogen ion) of azoles.

[0028] Moreover, by plating processing of the needlelike alloy which consists of copper-nickel-Lynn, they are a copper sulfate 1 – 40 g/l, and a nickel sulfate. It is desirable to use the plating bath of the liquid presentation which consists of 0.1 – 6.0 g/l, a citric acid 10 – 20 g/l, hypophosphite 10 – 100 g/l, a 10–40g [./l.] boric acid, a surfactant 0.01 – 10 g/l.

[0029] In this invention, the complex of thermosetting resin, thermoplastics or thermosetting resin, and thermoplastics can be used as a resin insulating layer between layers used by the build up wiring layer. As thermosetting resin, an epoxy resin, polyimide resin, phenol resin, thermosetting polyphenylene ether (PPE), etc. can be used. As thermoplastics, polytetrafluoroethylene (PTFE), Fluororesins, such as an ethylene tetrafluoride 6 fluoride propylene copolymer (FEP) and an ethylene tetrafluoride perphloro alkoxy copolymer (PFA), Polyethylene terephthalate (PET), polysulfone (PSF), A polyphenylene sulfide (PPS), thermoplastic mold polyphenylene ether (PPE), Polyether sulfone (PES), polyether imide (PEI), polyphenylene sulfone (PPES), polyethylenenaphthalate (PEN), a polyether ether ketone (PEEK), polyolefine system resin, etc. can be used. Epoxy resin-PES, epoxy resin-PSF, epoxy resin-PPS, epoxy resin-PPES, etc. can be used as complex of thermosetting resin and thermoplastics.

[0030] In this invention, glass-fabrics impregnating resin complex can be used as a resin insulating layer between layers. As this glass-fabrics impregnating resin complex, there are

glass-fabrics sinking-in epoxy, glass-fabrics sinking-in bismaleimide triazine, glass-fabrics sinking [PTFE] in, glass-fabrics sinking [PPE] in, glass-fabrics sinking-in polyimide, etc.

[0031] Moreover, in this invention, the adhesives for nonelectrolytic plating can be used as a resin insulating layer between layers. The thing which it comes to distribute in the heat resistant resin which is not hardened [from which the heat-resistant-resin particle of fusibility becomes the acid or oxidizer by which hardening processing was carried out with poor solubility by hardening processing as these adhesives for nonelectrolytic plating at an acid or an oxidizer] is the optimal. a heat-resistant-resin particle carries out dissolution removal of this reason by processing with an acid or an oxidizer -- having -- a front face -- an octopus -- it is because the roughening side which consists of end-crater-like support can be formed. The depth of a roughening side has good 0.01-20 micrometers. It is for securing adhesion. Moreover, also in a semi additive process, 0.1-5 micrometers is good. It is because it is the range which can remove the nonelectrolytic plating film, securing adhesion.

[0032] In the above-mentioned adhesives for nonelectrolytic plating, as said heat-resistant-resin particle by which especially hardening processing was carried out ** The floc which heat-resistant-resin powder 10 micrometers or less and ** mean particle diameter made condense [mean particle diameter] heat-resistant-resin powder 2 micrometers or less, The heat-resistant-resin powder and mean particle diameter whose mean particle diameter is 2-10 micrometers ** Mixture with heat-resistant-resin powder 2 micrometers or less, ** The false particle to which mean particle diameter makes one sort come to adhere to it even if the front face of heat-resistant-resin powder whose mean particle diameter is 2-10 micrometers has little heat-resistant-resin powder 2 micrometers or less or inorganic powder either, ** mean particle diameter 0.1-0.8 The heat-resistant-resin powder and mean particle diameter of mum 0.8 micrometers -- exceeding -- mixture with less than 2-micrometer heat-resistant-resin powder, and ** mean particle diameter 0.1-1.0 the heat-resistant-resin powder of mum -- since -- even if few either, the thing which is chosen and which use one sort is desirable. These are because more complicated support can be formed. The complex of the above-mentioned thermosetting resin, thermoplastics, thermosetting resin, and thermoplastics can be used for the heat resistant resin used with these adhesives for nonelectrolytic plating.

[0033] the conductor formed in this invention on the conductor layer (a wrap thing is included for the filler with which the through hole was filled up) formed on the substrate, and the resin insulating layer between layers -- a circuit is connectable in the Bahia hall. In this case, as for the Bahia hall, what was filled up with the plating film or conductive paste is good.

[0034] Next, an example is given and how to manufacture the multilayer printed wiring board of this invention is explained concretely. In addition, although the approach described below is related with the manufacture approach of the multilayer printed wiring board by the semiadditive process, by the manufacture approach of the multilayer printed wiring board in this invention, a fully-additive process, a multi-lamination process, and the pin lamination method can be used for it.

[0035] (1) First, break a through tube with a drill in a substrate, perform nonelectrolytic plating to the substrate front face containing the internal surface of a through tube, and form a through hole in it. As a substrate, resin substrates, such as a glass epoxy group plate, a polyimide substrate, a bismaleimide-triazine resin substrate, and a fluororesin substrate, or the copper clad laminate of these resin, a ceramic substrate, a metal substrate, etc. can be used. Especially when taking a dielectric constant into consideration, it is desirable to use double-sided copper-clad fluororesin substrates (polytetrafluoroethylene etc.). This substrate carries out thermocompression bonding of the copper foil by which one side was roughened to a fluororesin substrate. As nonelectrolytic plating, copper plating is good. when the covering power of plating is a bad substrate like a fluororesin substrate, surface treatment using the pretreatment liquid (trade name: -- tetra-- dirty) which consists of an organic acid etc., such as processing and plasma treatment, is performed.

[0036] (2) Next, perform electrolysis plating for thickness attachment. As this electrolysis plating, copper plating is good. And further, roughening processing of a through hole wall and the electrolysis plating film front face may be carried out, and a roughening layer may be prepared.

There is what is depended on oxidation (melanism)-reduction processing, a thing which carried out spray processing (etching processing) and formed the mixed water solution of an organic acid and the second copper complex, or a thing to depend on a copper-nickel-Lynn needlelike alloy plating in this roughening layer.

[0037] When forming a roughening layer with nonelectrolytic plating in these processings, copper ion concentration, nickel ion concentration, and hypophosphorous acid ion concentration are each. It is desirable to use the plating water solution of the presentation which are 2.2×10^{-2} – 4.1×10^{-2} mol/l, 2.2×10^{-3} – 4.1×10^{-3} mol/l, and 0.20 – 0.25 mol/l. It is because the crystal structure of the coat which deposits in this range turns into needlelike structure and it excels in an anchor effect. In addition to the above-mentioned compound, a complexing agent and an additive may be added to this nonelectrolytic plating water solution. Moreover, a 0.01–10g [/.] surfactant may be added. as this surfactant — Nissin Chemical Industry SAFI Norian 440 for example, 465, and 485 etc. — it is desirable to use an acetylene content polyoxyethylene system surfactant. That is, when forming a roughening layer with nonelectrolytic plating, they are a copper sulfate 1 – 40 g/l, and a nickel sulfate. It is desirable to use the plating water solution of the liquid presentation which consists of 0.1 – 6.0 g/l, a citric acid 10 – 20 g/l, hypophosphite 10 – 100 g/l, a boric acid 10 – 40 g/l, and a surfactant 0.01 – 10 g/l.

[0038] When forming a roughening layer by oxidation reduction processing, it is desirable to make NaOH (20 g/l), NaClO₂ (50 g/l), and Na₃PO₄ (15.0 g/l) into an oxidation bath, and to make NaOH (2.7 g/l) and NaBH₄ (1.0 g/l) into a reduction bath.

[0039] Although it is represented by MEC COMPANY LTD. CZ8100 liquid when forming a roughening layer by etching processing using the mixed water solution of an organic acid and the second copper complex, a copper front face is made into irregularity using the oxidizing power of the divalent copper contained in liquid.

[0040] The roughening layer may be covered with the layer of the metal whose ionization tendency is below titanium more greatly than copper, or noble metals. the time of the layer of said metal or noble metals covering a roughening layer, and this reason carrying out roughening processing of the layer insulation layer — a conductor — the local electrode reaction of a circuit — preventing — that conductor — it is because the dissolution of a circuit is prevented. The thickness of this layer has good 0.01–2 micrometers. As such a metal, there is at least one sort chosen from titanium, aluminum, zinc, iron, an indium, a thallium, cobalt, nickel, tin, lead, and a bismuth. Moreover, there are gold, silver, platinum, and palladium as noble metals. Especially, since tin can form a film with non-electrolyzed permutation plating and can follow a roughening layer, it is advantageous. In the case of this tin, hoe stannous-fluoride-thiourea and tin chloride-thiourea liquid are used and about 0.01–2-micrometer Sn layer is formed of the substitution reaction of Cu–Sn. On the other hand, as for the case of noble metals, approaches, such as a spatter and vacuum evaporatio, are adopted.

[0041] (3) Next, it is filled up with the filler of a configuration of having mentioned above in a through hole. By applying in print processes on the substrate which laid the mask which prepared opening in the through hole part, it fills up with a filler in a through hole, and, specifically, it is dried and hardened after restoration. As hardening conditions, it is at 50 – 160 **. It is desirable that it is 0.5 – 5 hours.

[0042] Furthermore, polish removes the roughening layer of the electrolysis plating film front face of the filler and substrate overflowing from a through hole, and flattening of the substrate front face is carried out. This polish has a belt sander and good buffing. Some metal particles are exposed to a front face, this exposed plating coat of the metal particles of a part and a conductor layer unifies, and good adhesion is discovered with this polish.

[0043] (4) Above (3) After giving a catalyst nucleus to the front face of the substrate which carried out flattening, nonelectrolytic plating is performed, and it is thickness. The about 0.1–5-micrometer nonelectrolytic plating film is formed, electrolysis plating is performed further if needed, and the electrolysis plating film with a thickness of 5–25 micrometers is prepared. Next, a photosensitive dry film is laminated by hot press, the photo-mask film (glass is good) with which the pattern was drawn is laid, after exposing on the front face of the plating film, negatives are developed on it with a developer and etching resist is prepared in it. and the thing done for

the dissolution removal of the conductor of an etching-resist agenesis part with an etching reagent -- a conductor -- a wrap conductor-layer part is formed for a circuit part and a filler. As the etching reagent, persulfate water solutions, such as a water solution of a sulfuric-acid-hydrogen peroxide, ammonium persulfate, and sodium persulfate, potassium persulfate, and the water solution of a ferric chloride or a cupric chloride are good.

[0044] (5) and the conductor which exfoliated and became independent about etching resist -- the conductor after considering as a circuit and a conductor layer -- form a roughening layer in a circuit and the front face of a conductor layer. a conductor -- since the conductor is excellent in adhesion with the resin insulating layer between layers in a circuit and a filler when a roughening layer is formed in the front face of a wrap conductor layer -- a conductor -- the crack on the basis of the interface of the side face of a wrap conductor layer and a resin insulating layer does not generate a circuit and a filler. Moreover, by one side, adhesion with the Bahia hall where a wrap conductor layer is connected electrically is improved in a filler. The formation approach of this roughening layer is as having mentioned above, and has oxidation (melanism)-reduction processing, a needlelike alloy plating, or the approach of etching and forming. furthermore, after roughening -- a conductor -- it may be filled up with resin between circuits, and a front face may be ground and graduated. in this case, after polish -- a conductor -- it is desirable to roughen a circuit front face. As restoration resin at this time, they are a bisphenol female mold epoxy resin, an imidazole curing agent, and mean particle diameter. The constituent which consists of a 0.1-30-micrometer inorganic particle is good.

[0045] (6) Form the resin insulating layer between layers on the wiring substrate which carried out in this way and was produced. As a resin insulating layer between layers, the complex of thermosetting resin, thermoplastics or thermosetting resin, and thermoplastics can be used. Moreover, in this invention, the adhesives for nonelectrolytic plating mentioned above as a resin insulating material between layers can be used. The resin insulating layer between layers is formed by applying the non-sclerosing solution of these resin using a roll coater, curtain coater, etc., or carrying out thermocompression bonding of the film-like resin, and laminating it. in addition -- this condition -- a conductor -- the conductor in which the resin insulation layer thickness between layers on a circuit pattern is thin, and has a large area -- since the resin insulation layer thickness between layers on a circuit became thick and irregularity has occurred in many cases, it is desirable to press using a metal plate metallurgy group roll, heating, and to carry out flattening of the front face of the resin insulating layer between layers.

[0046] (7) next, the lower layer conductor covered by this resin insulating layer between layers -- in order to secure electrical installation with a circuit (through hole), prepare opening in the resin insulating layer between layers. Punching of this opening is performed in exposure and a development, when the resin insulating layer between layers consists of a photopolymer, and when consisting of thermosetting resin or thermoplastics, it is performed in a laser beam. At this time, there are carbon dioxide gas laser, ultraviolet laser, excimer laser, etc. as a laser beam used. DESUMIA processing may be performed when hole dawn is carried out in a laser beam. It can carry out using the oxidizer which consists of water solutions, such as a chromic acid and a permanganate, and this DESUMIA processing is the oxygen plasma, oxygen, and CF4. You may process with the mixed-gas plasma etc.

[0047] (8) Roughen the front face of the resin insulating layer between layers in which opening was formed, if needed. When the adhesives for nonelectrolytic plating mentioned above are used as a resin insulating layer between layers, the front face of the insulating layer is processed with an acid or an oxidizer, it dissolves or removes [decomposition] alternatively and only a heat-resistant-resin particle is roughened. As an acid, although there are organic acids, such as a phosphoric acid, a hydrochloric acid, a sulfuric acid or formic acid, and an acetic acid, it is desirable to use especially an organic acid. It is because it is hard to make the metallic conductor layer exposed from the Bahia hall corrode when roughening processing is carried out. As an oxidizer, it is desirable to use a chromic acid and permanganates (potassium permanganate etc.). Moreover, even when thermosetting resin and thermoplastics are used, the surface roughening processing by the oxidizer chosen from water solutions, such as a chromic acid and a permanganate, is effective. in addition, the case of resin, such as fluororesins

(polytetrafluoroethylene etc.) which are not roughened in an oxidizing agent, -- plasma treatment -- tetra-- a front face is roughened by it being dirty (Junkosha metal naphthalene compound) etc.

[0048] (9) Next, give the catalyst nucleus for nonelectrolytic plating to the roughening side of said resin insulating layer between layers. Generally, a catalyst nucleus is palladium-tin colloid, immerses for it, dries and heat-treats a substrate in this solution, and fixes a catalyst nucleus to a resin front face. Moreover, a metal nucleus can be driven into a resin front face by CVD, the spatter, and the plasma, and it can consider as a catalyst nucleus. in this case, a metal nucleus is embedded on a resin front face -- ***** -- a core [nucleus / this / metal] -- plating -- depositing -- a conductor -- the resin which is hard to roughen since a circuit is formed, and fluororesins (polytetrafluoroethylene etc.) -- like -- resin and a conductor -- bad resin can also secure [adhesion with a circuit] adhesion. As this metal nucleus, any which are chosen from palladium, silver, gold, platinum, titanium, copper, and nickel or at least one or more sorts are good. In addition, the amount of a metal nucleus is 20microg/cm². The following is good. It is because a metal nucleus must be removed if this amount is exceeded.

[0049] (10) Next, perform nonelectrolytic plating to the roughening side of the resin insulating layer between layers, and form the nonelectrolytic plating film in the whole surface. thickness of this nonelectrolytic plating film 0.1-5 micrometers -- more -- desirable -- It is 0.5-3 micrometers. Non-electrolytic copper plating of nonelectrolytic plating is good. As the plating liquid, the thing of a conventional method can be used, for example, they are a 29g [/l.] copper sulfate, the sodium carbonate of 25 g/l, the tartrate of 140 g/l, the sodium hydroxide of 40 g/l, and 37% formaldehyde. The thing of the presentation which consists of 150ml and pH=11.5 is good.

[0050] (11) Form plating resist on the nonelectrolytic plating film formed above (10). As mentioned above, plating resist laminates a photopolymer film (dry film), and is formed exposure and by carrying out a development.

[0051] (12) -- further -- a plating-resist agenesis part -- electrolysis plating -- giving -- a conductor -- a circuit part (the Bahia hall part is included) is thickness-attached, and is carried out. As the above-mentioned electrolysis plating, it is desirable to use copper plating here, and the thickness has good 5-30 micrometers. Moreover, it is desirable for it to be filled up with the electrolysis plating film and to form the so-called fill DOBIA in said Bahia hall. This reason is that the surface smoothness of the resin insulating layer between layers is securable. Furthermore, said Bahia hall may be formed in right above [of the through hole established in the substrate]. It is for densification.

[0052] (13) the conductor which carried out dissolution removal of the nonelectrolytic plating film under the plating resist with etching reagents, such as persulfate water solutions, such as a mixed water solution of a sulfuric acid and a hydrogen peroxide, sodium persulfate, ammonium persulfate, and sodium persulfate, potassium persulfate, and a ferric chloride, a water solution of a cupric chloride, and became independent after exfoliating plating resist -- consider as a circuit (the Bahia hall is included). Furthermore, dissolution removal of the palladium catalyst nucleus on the exposed roughening side is carried out by a chromic acid etc.

[0053] (14) and the process of the above-mentioned [top / this / substrate] -- repeating -- further -- the upper conductor -- a circuit can be prepared. Hereafter, it explains based on an example.

[0054]

[Example] (Example 1)

(1) Thickness Copper clad laminate which the 18-micrometer copper foil 2 by which one side roughening was carried out laminates in 0.8mm BT (bismaleimide triazine) resin substrate 1 was used as the start ingredient (refer to drawing 1 (a)). First, carried out drill drilling of this copper clad laminate (refer to drawing 1 (b)), subsequently palladium-tin colloid was made to adhere, and nonelectrolytic plating was performed on the following presentation and conditions.

[Nonelectrolytic plating water solution]

EDTA 150 g/l copper sulfate 20 g/lHCHO 30 ml/INaOH 40 g/lalpha and alpha'-bipyridyl 80 mg/IPEG 0.1 g/l [nonelectrolytic plating conditions]

It is 30 minutes [0055] by whenever [70-degree C solution temperature]. Subsequently, electrolytic copper plating was performed on condition that the following, and the electrolytic copper plating film with a thickness of 15 micrometers was formed (refer to drawing 1 (c)).

[Electrolysis plating water solution]

Sulfuric acid 180 g/l Copper sulfate 80 g/l Additive (made in ATOTEKKU Japan, a trade name: KAPARASHIDO GL)

1 MI/l [Electrolysis Plating Conditions]

Current density 1 A/dm² 2 hours 30-minute temperature Room temperature [0056] (2) The substrate in which the conductor (a through hole is included) which consists of non-electrolytic copper plating film and electrolytic copper plating film was formed on the whole surface NaOH (20 g/l), NaClO₂ after washing in cold water and drying (50 g/l), The oxidation reduction processing which makes a reduction bath an oxidation bath (melanism bath), NaOH (2.7 g/l), and NaBH₄ (1.0 g/l) was presented with Na₃PO₄ (15.0g/(l)), and the roughening layer 4 was formed in all the front faces of a conductor including the through hole 3 (refer to drawing 1 (d)).

[0057] [preparation of the filler for through holes] -- a cresol novolak mold epoxy resin (the product made from oil-ized shell --) the Epicoat 152 3.5 weight section and a bisphenol female mold epoxy resin (the product made from oil-ized shell --) The Epicoat 807 14.1 weight section and the silica superfines end of 14nm mean particle diameter (Aerosil R202) The 1.0 weight sections are kneaded with 3 rollers. Furthermore, imidazole curing agent (Shikoku formation make, 2E4 MZ-CN) The 1.2 weight sections, Copper powder with a mean particle diameter of 15 micrometers The 100 weight sections are added, and it kneads with 3 rollers, and is at 22**1 degree C about the viscosity of such mixture. It adjusted to 200 - 1000 Pa-s, and the filler 5 for through holes was prepared.

[0058] (3) They are every 1 hour and a pan, respectively at 80 degrees C after being filled up with the prepared filler 5 by screen-stencil in a through hole 3 and drying, and 100 **. It was made to harden with heating of 1 hour at 150 degrees C. and a conductor -- the filler 5 which it began to see from a roughening side and a through hole 3 on top -- #400 The belt sander polish using belt abrasive paper (Sankyo Rikagaku make) removed, further, in order to remove the blemish by this belt sander polish, buffing by the alumina abrasive grain or the SiC abrasive grain was performed, and flattening of the substrate front face was carried out (refer to drawing 1 (e)).

[0059] (4) Above (3) A palladium catalyst (product made from ATOTEKKU) is given to the substrate front face which carried out flattening, and it is the above (1). By performing non-electrolytic copper plating on the same conditions, it is thickness. The 0.6-micrometer non-electrolytic copper plating film 6 was formed (refer to drawing 1 (f)).

[0060] (5) subsequently, the above (1) the same conditions -- electrolytic copper plating -- giving -- the electrolytic copper plating film 7 with a thickness of 15 micrometers -- forming -- a conductor -- the thickness of the part used as a circuit 9 -- the part which serves as the wrap conductor layer (circular through hole land) 10 in the filler 5 with which attached and the through hole 3 was filled up was formed.

[0061] (6) a conductor -- a commercial photosensitive dry film is stuck on both sides of the substrate in which the part used as a circuit 9 and a conductor layer 10 was formed, and a mask is laid in them -- 100 mJ/cm² The development was carried out in exposure and a 0.8% sodium-carbonate water solution, and the etching resist 8 with a thickness of 15 micrometers was formed (refer to drawing 2 (a)).

[0062] (7) the conductor which carried out dissolution removal of the plating film of the part which does not form etching resist 8 with the etching reagent using the mixed liquor of a sulfuric acid and a hydrogen peroxide, carried out exfoliation removal of the etching resist 8 by KOH 5% further, and became independent -- the wrap conductor layer 10 was formed for the circuit 9 and the filler 5 (refer to drawing 2 (b)). furthermore, the conductor which carries out oxidation reduction processing and includes a side face -- a front face -- the above (2) Roughening processing was carried out similarly.

[0063] [Preparation of a resin bulking agent]

** . Bisphenol female mold epoxy monomer (product made from oil-ized shell, molecular weight

310, YL983U) 100 weight section, Mean-particle-diameter spherical particle by which coating of the silane coupling agent was carried out to the front face It is SiO₂ at 1.6 micrometers (the product made from an ADOMA tech, CRS 1101-CE, and here). magnitude of grain of maximum size is made below into the thickness (15 micrometers) of the inner layer copper pattern mentioned later -- the 170 weight sections and leveling agent (the Sannopuko make, PERENORU S4) The 1.5 weight sections are kneaded with 3 rolls. It is 45,000-49,000cps at 23**1 degree C about the viscosity of the mixture. It adjusted.

** . Imidazole curing agent 6.5 (Shikoku formation make, 2E4 MZ-CN) Weight section. These were mixed and resin bulking agent 12a was prepared.

[0064] (8) applying prepared resin bulking agent 12a to one side of a substrate by screen-stencil -- a conductor -- it is filled up between a circuit 9 or a conductor layer 10, and dries in 70 degrees C and 20 minutes -- making -- the field of another side -- the same -- carrying out -- resin bulking agent 12a -- a conductor -- it was filled up between the circuit 9 or the conductor layer 10, and was made to dry in 70 degrees C and 20 minutes That is, this process is filled up with resin bulking agent 12a between inner layer copper patterns.

[0065] (9) Above (8) It is one side of a substrate which finished processing #400 By belt sander polish using belt abrasive paper (Sankyo Rikagaku make), it ground so that resin bulking agent 12a might not remain in the front face of the inner layer copper patterns 9 and 10, and subsequently buffing for removing the blemish by said belt sander polish was performed. Such a series of polishes were similarly performed about the field of another side of a substrate. Subsequently, 120 degree C performed [100 degree C] heat-treatment of 7 hours at 180 degree C by 150 degree C for 1 hour for 3 hours for 1 hour, and resin bulking agent 12a was hardened.

[0066] thus, a conductor -- the surface section of resin bulking agent 12a with which it filled up between the circuit 9 or the conductor layer 10, and a conductor -- the roughening layer 11 of a circuit 9 or conductor-layer 10 top face -- removing -- substrate both sides -- graduating -- resin bulking agent 12a and a conductor -- the substrate which the circuit 9 or the side face of a conductor layer 10 stuck firmly through the roughening layer 11 was obtained. That is, the front face of resin bulking agent 12a and the front face of a inner layer copper pattern turn into the same flat surface according to this process. Tg point of filled hardening resin was [here,] 155.6 **, and the line coefficient of thermal expansion was 44.5×10^{-6} /degree C.

[0067] (10) next, a conductor -- thickness it is thin on the front face of the wrap conductor layer 10 from a Cu-nickel-P alloy in a circuit 9 and the front face of a filler 5 the 2.5-micrometer roughening layer (concave convex layer) 11 -- forming -- further -- the front face of this roughening layer 11 -- thickness 0.3-micrometer Sn layer was formed (not shown about refer to drawing 2 (c) and Sn layer). The formation approach is as follows. Namely, carry out acid cleaning of the substrate, and carry out software etching and, subsequently it processes with the catalyst solution which consists of a palladium chloride and an organic acid. Copper-sulfate 8 g/l, a nickel sulfate after giving Pd catalyst and activating this catalyst 0.6 g/l, citric-acid 15 g/l, sodium hypophosphite 29 g/l, boric-acid 31 g/l, and surfactant 0.1 g/l and the nonelectrolytic plating bath which consists of pH=9 -- plating -- giving -- copper -- a conductor -- thickness it is thin from a Cu-nickel-P alloy on the surface of a circuit The 2.5-micrometer roughening layer 11 was formed. Furthermore, pH=1.2 which consists of 0.1 mol/l hoe stannous-fluoride-1.0 mol/l thiourea liquid At the temperature of 50 degrees C, it is immersed in a non-electrolyzed tin permutation plating bath for 1 hour, a Cu-Sn substitution reaction is carried out to it, and it is thickness to the front face of said roughening layer. 0.3-micrometer Sn layer was prepared (not shown about Sn layer).

[0068] (11) The adhesives A and B for nonelectrolytic plating were prepared as follows.

A. They are 35 weight sections, the photosensitive monomer (Toagosei make and ARONIKKUSU M315) 3.15 weight section, and a defoaming agent (the Sannopuko make, S-65) about 25% acrylic ghost of the preparation **. cresol novolak mold epoxy resin (the Nippon Kayaku make, molecular weight 2500) of the adhesives for nonelectrolytic plating for the upper layers. The 0.5 weight sections and NMP Stirring mixing of the 3.6 weight sections was carried out.

** . The polyether sulfone (PES) 12 weight section, mean particle diameter of an epoxy resin

particle (Mitsuhiro formation make, the polymer pole) 1.0 micrometers The 7.2 weight sections, mean particle diameter After mixing the 3.09 weight sections for a 0.5-micrometer thing, the NMP30 weight section was added further and stirring mixing was carried out with the bead mill. ** . The imidazole curing agent (Shikoku formation make, 2E4 MZ-CN) 2 weight section, the photoinitiator (product made from Kanto chemistry, benzophenone) 2 weight section, and photosensitizer (the product made from the Hodogaya chemistry, and EAB) 0.2 Stirring mixing of the weight section and the NMP 1.5 weight section was carried out. These were mixed and the adhesives for nonelectrolytic plating for the upper layers were obtained.

[0069] B. They are 35 weight sections, the photosensitive monomer (Toagosei make and ARONIKKUSU M315) 4 weight section, and a defoaming agent (the Sannopuko make, S-65) about 25% acrylic ghost of the preparation **. cresol novolak mold epoxy resin (the Nippon Kayaku make, molecular weight 2500) of the adhesives for nonelectrolytic plating for lower layers. The 0.5 weight sections and NMP Stirring mixing of the 3.6 weight sections was carried out.

** . The polyether sulfone (PES) 12 weight section, mean particle diameter of an epoxy resin particle (Mitsuhiro formation make, the polymer pole) 0.5-micrometer thing After mixing the 14.49 weight sections, the NMP30 weight section was added further and stirring mixing was carried out with the bead mill.

** . The imidazole curing agent (Shikoku formation make, 2E4 MZ-CN) 2 weight section, the photoinitiator (Ciba-Geigy make, IRUGA cure I-907) 2 weight section, and photosensitizer (the Nippon Kayaku make, DETX-S) Stirring mixing of the 0.2 weight sections and the NMP 1.5 weight section was carried out. These were mixed and the adhesives for nonelectrolytic plating for lower layers were obtained.

[0070] (12) adhesives B for nonelectrolytic plating (viscosity 1.5 – 3.2 Pa·s) prepared above (11) Adhesives A for nonelectrolytic plating (viscosity 5 – 20 Pa·s) After using and applying the roll coater to both sides of a substrate one by one and leaving it to them for 20 minutes in the level condition, desiccation for 30 minutes was carried out to them at 60 degrees C, and with a thickness of 40 micrometers adhesives layer 12b (two-layer structure) was formed in them (refer to drawing 2 (d)). Furthermore, the polyethylene terephthalate film was stuck through the binder on this adhesives layer 12b.

[0071] (13) Stick the photo-mask film with which the black spot of 85 micrometerphi was printed to both sides of the substrate in which said adhesives layer 12b was formed, and it is an ultrahigh pressure mercury lamp. 500 mJ/cm² It exposed. By carrying out spray development of this with a DMDG solution, opening used as the Bahia hall of 85 micrometerphi was formed in adhesives layer 12b. Furthermore, it is the substrate concerned with an ultrahigh pressure mercury lamp 3000 mJ/cm² It exposes and is 1 hour and after that at 100 **. By carrying out heat-treatment of 5 hours at 150 degrees C, with a thickness of 35 micrometers adhesives layer (resin insulating layer between layers) 12b which has opening (opening 13 for the Bahia hall formation) excellent in the dimensional accuracy equivalent to a photo-mask film was formed (refer to drawing 2 (e)). In addition, a roughening layer is partially exposed to opening used as the Bahia hall.

[0072] (14) Dissolution removal of the epoxy resin particle which is immersed in a chromic acid for 19 minutes, and exists the substrate in which the opening 13 for the Bahia hall formation was formed in an adhesives layer front face was carried out, and the front face of the adhesives layer concerned was roughened, and after being immersed in the neutralization solution (product made from SHIPUREI) after that, it rinsed.

[0073] (15) The catalyst nucleus was given to the front face of adhesives layer 12b and the opening 13 for the Bahia halls by giving a palladium catalyst (product made from ATOTEKKU) to the substrate which performed the surface roughening process (a roughening depth of 3 micrometers).

[0074] (16) To this substrate, it is the above (1). Non-electrolytic copper plating was performed similarly and the non-electrolytic copper plating film with a thickness of 0.6 micrometers was formed in the whole split face (refer to drawing 3 (a)). At this time, since the plating film was thin, irregularity was observed in the nonelectrolytic plating film front face.

[0075] (17) a commercial photopolymer film (dry film) is stuck on the non-electrolytic copper plating film 14, and a mask is laid — 100 mJ/cm² it exposes — the development was carried out by the 0.8% sodium carbonate, and the plating resist 16 with a thickness of 15 micrometers was formed (refer to drawing 3 (b)).

[0076] (18) next, the above (1) the same — carrying out — electrolytic copper plating — giving — the electrolytic copper plating film 15 with a thickness of 15 micrometers — forming — a conductor — thickness attachment of a circuit part and the Bahia hall part was performed (refer to drawing 3 (c)).

[0077] (19) a conductor with a thickness of 16 micrometers which carries out etching processing of the nonelectrolytic plating film 14 under the plating resist 16 with the mixed liquor of a sulfuric acid and a hydrogen peroxide, carries out dissolution removal and consists of non-electrolytic copper plating film 14 and electrolytic copper plating film 15 after carrying out exfoliation removal of the plating resist 16 by KOH 5% — the circuit 9 (the Bahia hall 17 is included) was formed (refer to drawing 3 (d)).

[0078] (20) the above (19) — a conductor — the substrate in which the circuit 9 (the Bahia hall 17 is included) was formed — copper-sulfate 8 g/l and nickel sulfate 0.6 g/l, citric-acid 15 g/l, sodium hypophosphite 29 g/l, a 31g [l.] boric acid, and surfactant the nonelectrolytic plating liquid of pH=9 which consists of 0.1 g/l — being immersed — this — a conductor — the roughening layer 11 which consists of with a thickness of 3 micrometers copper-nickel-Lynn on the surface of a circuit was formed. When the roughening layer 11 was analyzed by EPMA (X-ray fluorescence) at this time, the presentation ratio of nickel 1.5mol % and P 0.5 mol% was shown Cu 98mol%. And further, the substrate was washed in cold water, it was immersed in the non-electrolyzed tin permutation plating bath which consists of 0.1 mol/l hoe ****-ized tin-1.0 mol/l thiourea liquid at 50 degrees C for 1 hour, and the tin permutation plating layer with a thickness of 0.05 micrometers was formed in the front face of said roughening layer 11 (however, not shown about a tin permutation plating layer).

[0079] (21) repeating the process of aforementioned (12) – (20) — further — the upper resin insulating-layer 12 between layers b, and a conductor — the one-layer laminating of the circuit 9 (the Bahia hall 17 is included) was carried out, and the multilayer-interconnection substrate was obtained (refer to drawing 4 (a)). in addition — here — a conductor — although the roughening layer 11 which consists of copper-nickel-Lynn on the surface of a circuit is formed, a tin permutation plating layer is not formed in this roughening layer 11 front face.

[0080] (22) Oligomer of the photosensitive grant which, on the other hand, acrylic-ized 50% of epoxy groups of 60% of the weight of the cresol novolak mold epoxy resin (Nippon Kayaku make) dissolved in DMDG (molecular weight 4000) The 46.67 weight sections, 80% of the weight of the bisphenol A mold epoxy resin (the product made from oil-ized shell —) dissolved in the methyl ethyl ketone the Epicoat 1001 14.121 weight section and an imidazole curing agent (Shikoku — formation — make —) the multiple-valued acrylic monomer (the Nippon Kayaku make —) which are the 2E4 MZ-CN1.6 weight section and a photosensitive monomer the R604 1.5 weight section — the same — a multiple-valued acrylic monomer (the product made from the Kyoisha chemistry —) the leveling agent (the Kyoisha make —) which consists of the DPE6A 3.0 weight section and an acrylic ester polymerization object The poly flow No.75 0.36 weight section is mixed, and it is the IRUGA cure I-907 (Ciba-Geigy make) as a photoinitiator to this mixture. The 2.0 weight sections, DETX-S as a photosensitizer (Nippon Kayaku make) The 0.2 weight sections are added and it is DMDG (diethylene-glycol wood ether)1.0 further. The weight section was added and the solder resist constituent which adjusted viscosity to 1.4**0.3 Pa·s at 25 degrees C was obtained. In addition, measurement of viscosity is a Brookfield viscometer (Tokyo Keiki and DVL-B mold). In the case of 60rpm, they are rotor No.4 and 6rpm. The case was based on rotor No.4.

[0081] (23) The above-mentioned solder resist constituent was applied to both sides of the multilayer-interconnection substrate obtained above (21) by the thickness of 20 micrometers. Subsequently, the side in which the chromium layer was formed in the soda lime glass substrate with a thickness of 5mm with which the circle pattern (mask pattern) of solder resist opening was drawn by the chromium layer after performing for 20 minutes at 70 degrees C and

performing desiccation processing for 30 minutes at 70 degrees C is stuck in a solder resist layer, and they are 1000 mJ/cm². The DMTG development was exposed and carried out by ultraviolet rays. Furthermore, it heat-treated at 120 degree C by 100 degree C for 1 hour for 1 hour, and heat-treated [80 degrees C] on the conditions of 3 hours by 150 degree C for 1 hour, and the solder resist (diameter of opening 200 micrometers) layer 18 (thickness of 20 micrometers) in which the pad part carried out opening was formed.

[0082] (24) Next, the substrate in which the solder resist layer 18 was formed was immersed in the non-electrolyzed nickel-plating liquid of pH=5 which consists of nickel chloride 30 g/l, sodium hypophosphite 10 g/l, and sodium-citrate 10 g/l for 20 minutes, and the nickel-plating layer 19 with a thickness of 5 micrometers was formed in opening. Furthermore, the substrate was immersed in the non-electrolyzed gilding liquid which consists of gold cyanide potassium 2 g/l, ammonium-chloride 75 g/l, sodium-citrate 50 g/l, and 10g [/l.] sodium hypophosphite for 23 seconds on 93-degree C conditions, and the gilding layer 20 with a thickness of 0.03 micrometers was formed on the nickel-plating layer 19.

[0083] (25) And print soldering paste to opening of the solder resist layer 18. By carrying out a reflow at 200 degrees C, the solder bump (solder object) 21 was formed and the multilayer printed wiring board which has the solder bump 21 was manufactured (refer to drawing 4 (b)). In addition, tin-silver, a tin-indium, tin-zinc, a tin-bismuth, etc. can be used as solder.

[0084] (Example 1 of a comparison) The multilayer printed wiring board which has a solder bump like an example 1 was manufactured except having made the through hole screen-stencil and harden conductive paste (the Tatsuta Electric Wire & Cable make, DD paste XAE1209).

[0085] Thus, about the multilayer printed wiring board of the manufactured example 1 and the example 1 of a comparison, it is humidity. 100%, temperature On the conditions of 121 degrees C and two atmospheric pressures The PCT (pressure cooker test) trial left for 200 hours was carried out, and the existence [through hole / the Bahia hall and] of an open circuit was checked. Consequently, with the patchboard of the example 1 of a comparison, the open circuit was seen to an open circuit not having been observed between the conductor layer and the through hole in the patchboard of an example 1. When this carries out the cross cut of the patchboard of the example 1 of a comparison in the through hole section and observes it with an optical microscope, conductive paste is carrying out hardening contraction, a clearance occurs between a through hole and the hardening object of the conductive paste, water collects here, and it serves as a gas with heating, pushes up the conductor layer on a through hole, and is presumed to have attained to the open circuit.

[0086]

[Effect of the Invention] As explained above, according to this invention, the printed wired board which controlled hardening contraction of a filler and secured the connection dependability of a through hole and the Bahia hall can be offered.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] Especially this invention is proposed about a multilayer printed wiring board about the multilayer printed wiring board which controlled hardening contraction of a filler and secured the connection dependability of a through hole and the Bahia hall.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] In recent years, the package substrate which mounts IC chip corresponds to the miniaturization or improvement in the speed of electronic equipment accompanying the advance of electronic industry, and the densification by the fine pattern and what has high dependability are called for.

[0003] As such a package substrate, a plating through hole is filled up with conductive paste, and the thing in which the conductor layer which covers this conductive paste was formed is indicated by JP,5-243728,A.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to this invention, the printed wired board which controlled hardening contraction of a filler and secured the connection dependability of a through hole and the Bahia hall can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in the package substrate concerning the conventional technique of upper **, since conductive paste was used, hardening contraction of the resin needed to be carried out and conductivity needed to be produced. For this reason, in this package substrate, when it was easy to produce the clearance resulting from hardening contraction of a filler between conductive paste and the conductor of a through hole wall and it put to the bottom of an elevated temperature and a humid condition, the problem that the conductor layer which covers conductive paste exfoliated, or an open circuit occurred a through hole, the Bahia hall, and in between arose.

[0005] Then, this invention aims at offering the printed wired board which controlled hardening contraction of a filler and secured the connection dependability of a through hole and the Bahia hall.

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MEANS

[Means for Solving the Problem] Artificers hit on an idea of the following contents to invention considered as a summary configuration, as a result of inquiring wholeheartedly towards implementation of the above-mentioned purpose.

(1) The multilayer printed wiring board of this invention on the substrate which has a conductor layer In the multilayer printed wiring board with which the build up wiring layer which carried out the laminating of the resin insulating layer between layers and the conductor layer by turns, and connected the conductor layers of an inside-and-outside layer in the Bahia hall is formed to said substrate The through hole which connects a front face and a rear face electrically is formed, the through hole is filled up with the non-conductive filler containing metal particles, and it is characterized by forming the wrap conductor layer in the exposure from the through hole of the filler further.

[0007] In addition, in the above-mentioned multilayer printed wiring board, it is desirable that the filler is connected to the wrap aforementioned conductor layer in the Bahia hall, and, as for said filler, it is desirable that metal particles, resin, and mean particle diameter consist of the inorganic superfines end of 1-1000nm preferably. Moreover, for said filler, specific resistance is 1×10^8 more desirably 1 or more M Ω -cm. It is more than Ω -cm and the mean particle diameter said metal particles It is desirable that it is 0.1-30 micrometers.

[0008]

[Embodiment of the Invention] the hardening contraction for giving conductivity to the filler containing metal particles, since a filler and its filler are excelled in adhesion with a wrap conductor layer since the filler which contains metal particles as an ingredient which fills a through hole is being used for the multilayer printed wiring board of such this invention, and the non-conductive filler is used -- it is not necessary to give -- a through hole wall -- exfoliation of the filler from a conductor can be prevented. It is because a conductor layer is pushed up and is made to exfoliate under heat-and-high-humidity conditions if such exfoliation exists, in case water collects and this water volatilizes.

[0009] It is desirable to use the constituent as for which metal particles, resin, and mean particle diameter become especially desirable as a filler from the inorganic superfines end of 1-1000nm (preferably 2-100nm) in this invention. The network structure in which this reason is formed of the intermolecular force after inorganic superfines carries out the trap of the metal particles, and those metal particles do not sediment. For this reason, it is because the conductor layer with which metal particles cover a projection, and this metal particles and it can unite with a filler front face and that adhesion can be raised. Exfoliation with a filler and a through hole conductor layer is prevented, and exfoliation with the conductor layer which covers a filler and this filler also with the bottom of heat-and-high-humidity conditions stops thereby, occurring.

[0010] Here, as metal particles which constitute said filler, copper, gold, silver, aluminum, nickel, titanium, chromium, tin/lead, palladium, etc. can be used. These metal particles may give metal surface treatment agents, such as a complexing agent, etc. to that front face, in order to improve adhesion with resin. That mean particle diameter these metal particles It is desirable that it is 0.1-30 micrometers. This reason is that it is the range which can secure adhesion with the conductor layer which covers a filler. Moreover, as for the loadings of these metal particles,

it is desirable to consider as 30 – 90 % of the weight to the total solids of a filler. This reason is that it is the range which can secure adhesion and printing nature to coincidence.

[0011] Moreover, thermosetting resin and thermoplastics can be used as matrix resin which constitutes said filler. As thermosetting resin, any or at least one sort of resin chosen from an epoxy resin, polyimide resin, and phenol resin is good. As thermoplastics, polytetrafluoroethylene (PTFE), Fluororesins, such as an ethylene tetrafluoride 6 fluoride propylene copolymer (FEP) and an ethylene tetrafluoride perfluoro alkoxy copolymer (PFA), Polyethylene terephthalate (PET), polysulfone (PSF), A polyphenylene sulfide (PPS), thermoplastic mold polyphenylene ether (PPE), Any which are chosen from polyether sulfone (PES), polyether imide (PEI), polyphenylene sulfone (PPES), polyethylenenaphthalate (PEN), a polyether ether ketone (PEEK), and polyolefine system resin or at least one sort is good.

[0012] it is chosen out of a bisphenol mold epoxy resin and a novolak mold epoxy resin as optimal resin especially used for a filler — one sort is good even if few either. When a bisphenol mold epoxy resin chooses resin, such as A mold and a female mold, suitably, even if a diluent solvent is not used for this reason, that viscosity can be adjusted, and a novolak mold epoxy resin is excellent in thermal resistance or chemical resistance with high intensity, and is not disassembled in a strong base nature solution like nonelectrolytic plating liquid, and it is because it does not pyrolyze. As said bisphenol mold epoxy resin, even if few either, the thing which is chosen from the bisphenol A mold epoxy resin and a bisphenol female mold epoxy resin and which use one sort is desirable. Especially, since a bisphenol female mold epoxy resin can be used with a non-solvent by hypoviscosity, it is advantageous. As said novolak mold epoxy resin, even if few either, the thing which is chosen from a phenol novolak mold epoxy resin and a cresol novolak mold epoxy resin and which use one sort is desirable. When blending and using a novolak mold epoxy resin and a bisphenol mold epoxy resin in such resin, the blending ratio of coal is 1 / 1 – 1/100 at a weight ratio. It is desirable. This reason is because it is the range which can prevent sedimentation of metal particles, controlling the rise of viscosity.

[0013] As an inorganic ultrafine particle which constitutes said filler, it is desirable to use a silica, an alumina, silicon carbide, and a mullite. A silica is the optimal especially. The mean particle diameter of this inorganic ultrafine particle is 2–100nm more preferably 1–1000nm. It carries out. This reason is that it is the range which can form association presumed to be hydrogen bond in the shape of a mesh, and can carry out the trap of the particulate matter, without spoiling the restoration nature of a through hole, since particle diameter is detailed. These loadings after inorganic superfines receive the total solids of a filler. It is desirable to consider as 0.1 – 5 % of the weight. This reason is that it is the range which can prevent hardening contraction, without spoiling restoration nature.

[0014] In addition, as a curing agent used for such a resin constituent, an imidazole system curing agent, an acid-anhydride curing agent, and an amine system curing agent are desirable. It is because hardening contraction is small. By controlling hardening contraction, it can really [of a filler and the conductor layer which covers it] turn, and the adhesion can be raised.

[0015] Moreover, the resin constituent before such hardening can be diluted with a solvent if needed. As this solvent, there are the cyclohexanol of NMP (normal methyl pyrrolidone), DMDG (diethylene-glycol wood ether), a glycerol, water, 1-, 2-, or 3-, a cyclohexanone, methyl Cellosolve, methyl Cellosolve acetate, a methanol, ethanol, a butanol, propanol, etc.

[0016] At this invention, it is the specific resistance of a filler 106 It is 108 more preferably more than omega-cm. It carries out to more than omega-cm, and considers as non-conductive. the time of grinding, after hardening that resin constituent if this reason makes a filler conductivity – – polish waste — a conductor — it is because it adheres between circuits and becomes a short cause. Moreover, although it is necessary to make it carry out hardening contraction that the above-mentioned resin constituent gives conductivity, it is because carrying out hardening contraction will cause exfoliation with the conductor layer which covers a filler, so it is not desirable.

[0017] In this invention, the through hole and the filler may be connected in the Bahia hall on the wrap conductor layer. This reason is that it can lose the dead space by the through hole.

[0018] In order to make a wiring consistency high in this invention, it is desirable to form the

conductor layer in the inner layer of a substrate. At this time, a substrate carries out the laminating of the prepreg to a conductor layer by turns, and it comes to form it. For example, a substrate carries out the laminating of the prepreg which resin was infiltrated into the cloth or nonwoven fabric of a glass fiber or an aramid fiber, and was made into B stage to copper foil or the circuit board by turns, and is formed by carrying out hot press and unifying.

[0019] the wall of the through hole where a filler is filled up with this invention -- a conductor -- it is desirable to form the roughening layer in a front face. This reason is that a filler and a through hole stick through a roughening layer, and a clearance does not occur. If an opening exists between a filler and a through hole, the conductor layer formed in right above [of it] with electrolysis plating will not become flat, or the air in an opening carries out thermal expansion of it, and it causes a crack and exfoliation, and is one side, and an opening is covered with water and it causes migration and a crack. If this point and a roughening layer are formed, such defect generating can be prevented.

[0020] moreover, this invention -- setting -- a filler -- the front face of a wrap conductor layer -- the conductor of a through hole wall -- it is advantageous that the roughening layer formed in the front face and the same roughening layer are formed. This reason is that adhesion with the resin insulating layer between layers or the Bahia hall is improvable with a roughening layer. If the roughening layer is especially formed in the side face of a conductor layer, the crack generated towards the resin insulating layer between layers with these interfaces as the starting point with the lack of adhesion of a conductor-layer side face and the resin insulating layer between layers can be controlled.

[0021] The thickness of the roughening layer formed in the front face of such a through hole wall or a conductor layer has good 0.1–10 micrometers. This reason is that it will become a short cause between layers if too thick, and the adhesion force with adherend will become low if too thin. What carried out oxidation (melanism)–reduction processing and formed the conductor of a through hole wall or the front face of a conductor layer as this roughening layer, the thing processed and formed with the mixed water solution of an organic acid and the second copper complex, or the thing formed by plating processing of a copper–nickel–Lynn needlelike alloy is good.

[0022] Let an oxidation bath (melanism bath), NaOH (2.7 g/l), and NaBH₄ (1.0 g/l.) be reduction baths for NaOH (20 g/l), NaClO₂ (50 g/l), and Na₃PO₄ (15.0 g/l) by the approach by oxidation (melanism)–reduction processing among these processings.

[0023] moreover -- the processing using the water solution of the organic–acid–second copper complex -- the bottom of oxygen coexistence conditions, such as a spray and bubbling, -- as follows -- acting -- a conductor -- metallic foils, such as copper which is a circuit, are dissolved.

$\text{Cu} + \text{Cu(II)} \text{ An} \rightarrow 2\text{Cu(I)} \text{ An}/2$ $2\text{Cu(I)} \text{ An}/2 + n/4 \text{O}_2 + n\text{AH}$ (aeration)
 $\rightarrow 2\text{Cu(II)} \text{ An} + n/2 \text{H}_2$ OA is a complexing agent.

[Translation done.]

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EXAMPLE

[Example] (Example 1)

(1) Thickness Copper clad laminate which the 18-micrometer copper foil 2 by which one side roughening was carried out laminates in 0.8mm BT (bismaleimide triazine) resin substrate 1 was used as the start ingredient (refer to drawing 1 (a)). First, carried out drill drilling of this copper clad laminate (refer to drawing 1 (b)), subsequently palladium-tin colloid was made to adhere, and nonelectrolytic plating was performed on the following presentation and conditions.

[Nonelectrolytic plating water solution]

EDTA 150 g/l copper sulfate 20 g/l HCHO 30 ml/l NaOH 40 g/l alpha and alpha'-bipyridyl 80 mg/l IPEG 0.1 g/l [nonelectrolytic plating conditions]

It is 30 minutes [0055] by whenever [70-degree C solution temperature]. Subsequently, electrolytic copper plating was performed on condition that the following, and the electrolytic copper plating film with a thickness of 15 micrometers was formed (refer to drawing 1 (c)).

[Electrolysis plating water solution]

Sulfuric acid 180 g/l Copper sulfate 80 g/l Additive (made in ATOTEKKU Japan, a trade name: KAPARASHIDO GL)

1 MI/l [Electrolysis Plating Conditions]

Current density 1 A/dm² 2 hours 30-minute temperature Room temperature [0056] (2) The substrate in which the conductor (a through hole is included) which consists of non-electrolytic copper plating film and electrolytic copper plating film was formed on the whole surface NaOH (20 g/l), NaClO₂ after washing in cold water and drying (50 g/l), The oxidation reduction processing which makes a reduction bath an oxidation bath (melanism bath), NaOH (2.7 g/l), and NaBH₄ (1.0 g/l) was presented with Na₃PO₄ (15.0g/l), and the roughening layer 4 was formed in all the front faces of a conductor including the through hole 3 (refer to drawing 1 (d)).

[0057] [preparation of the filler for through holes] -- a cresol novolak mold epoxy resin (the product made from oil-ized shell --) the Epicoat 152 3.5 weight section and a bisphenol female mold epoxy resin (the product made from oil-ized shell --) The Epicoat 807 14.1 weight section and the silica superfines end of 14nm mean particle diameter (Aerosil R202) The 1.0 weight sections are kneaded with 3 rollers. Furthermore, imidazole curing agent (Shikoku formation make, 2E4 MZ-CN) The 1.2 weight sections, Copper powder with a mean particle diameter of 15 micrometers The 100 weight sections are added, and it kneads with 3 rollers, and is at 22**1 degree C about the viscosity of such mixture. It adjusted to 200 - 1000 Pa-s, and the filler 5 for through holes was prepared.

[0058] (3) They are every 1 hour and a pan, respectively at 80 degrees C after being filled up with the prepared filler 5 by screen-stencil in a through hole 3 and drying, and 100 **. It was made to harden with heating of 1 hour at 150 degrees C. and a conductor -- the filler 5 which it began to see from a roughening side and a through hole 3 on top -- #400 The belt sander polish using belt abrasive paper (Sankyo Rikagaku make) removed, further, in order to remove the blemish by this belt sander polish, buffing by the alumina abrasive grain or the SiC abrasive grain was performed, and flattening of the substrate front face was carried out (refer to drawing 1 (e)).

[0059] (4) Above (3) A palladium catalyst (product made from ATOTEKKU) is given to the

substrate front face which carried out flattening, and it is the above (1). By performing non-electrolytic copper plating on the same conditions, it is thickness. The 0.6-micrometer non-electrolytic copper plating film 6 was formed (refer to drawing 1 (f)).

[0060] (5) subsequently, the above (1) the same conditions -- electrolytic copper plating -- giving -- the electrolytic copper plating film 7 with a thickness of 15 micrometers -- forming -- a conductor -- the thickness of the part used as a circuit 9 -- the part which serves as the wrap conductor layer (circular through hole land) 10 in the filler 5 with which attached and the through hole 3 was filled up was formed.

[0061] (6) a conductor -- a commercial photosensitive dry film is stuck on both sides of the substrate in which the part used as a circuit 9 and a conductor layer 10 was formed, and a mask is laid in them -- 100 mJ/cm² The development was carried out in exposure and a 0.8% sodium-carbonate water solution, and the etching resist 8 with a thickness of 15 micrometers was formed (refer to drawing 2 (a)).

[0062] (7) the conductor which carried out dissolution removal of the plating film of the part which does not form etching resist 8 with the etching reagent using the mixed liquor of a sulfuric acid and a hydrogen peroxide, carried out exfoliation removal of the etching resist 8 by KOH 5% further, and became independent -- the wrap conductor layer 10 was formed for the circuit 9 and the filler 5 (refer to drawing 2 (b)). furthermore, the conductor which carries out oxidation reduction processing and includes a side face -- a front face -- the above (2) Roughening processing was carried out similarly.

[0063] [Preparation of a resin bulking agent]

** . Bisphenol female mold epoxy monomer (product made from oil-ized shell, molecular weight 310, YL983U) 100 weight section, Mean-particle-diameter spherical particle by which coating of the silane coupling agent was carried out to the front face It is SiO₂ at 1.6 micrometers (the product made from an ADOMA tech, CRS 1101-CE, and here). magnitude of grain of maximum size is made below into the thickness (15 micrometers) of the inner layer copper pattern mentioned later -- the 170 weight sections and leveling agent (the Sannopuko make, PERENORU S4) The 1.5 weight sections are kneaded with 3 rolls. It is 45,000-49,000cps at 23**1 degree C about the viscosity of the mixture. It adjusted.

** . Imidazole curing agent 6.5 (Shikoku formation make, 2E4 MZ-CN) Weight section. These were mixed and resin bulking agent 12a was prepared.

[0064] (8) applying prepared resin bulking agent 12a to one side of a substrate by screen-stencil -- a conductor -- it is filled up between a circuit 9 or a conductor layer 10, and dries in 70 degrees C and 20 minutes -- making -- the field of another side -- the same -- carrying out -- resin bulking agent 12a -- a conductor -- it was filled up between the circuit 9 or the conductor layer 10, and was made to dry in 70 degrees C and 20 minutes That is, this process is filled up with resin bulking agent 12a between inner layer copper patterns.

[0065] (9) Above (8) It is one side of a substrate which finished processing #400 By belt sander polish using belt abrasive paper (Sankyo Rikagaku make), it ground so that resin bulking agent 12a might not remain in the front face of the inner layer copper patterns 9 and 10, and subsequently buffing for removing the blemish by said belt sander polish was performed. Such a series of polishes were similarly performed about the field of another side of a substrate. Subsequently, 120 degree C performed [100 degree C] heat-treatment of 7 hours at 180 degree C by 150 degree C for 1 hour for 3 hours for 1 hour, and resin bulking agent 12a was hardened.

[0066] thus, a conductor -- the surface section of resin bulking agent 12a with which it filled up between the circuit 9 or the conductor layer 10, and a conductor -- the roughening layer 11 of a circuit 9 or conductor-layer 10 top face -- removing -- substrate both sides -- graduating -- resin bulking agent 12a and a conductor -- the substrate which the circuit 9 or the side face of a conductor layer 10 stuck firmly through the roughening layer 11 was obtained. That is, the front face of resin bulking agent 12a and the front face of a inner layer copper pattern turn into the same flat surface according to this process. Tg point of filled hardening resin was [here,] 155.6 **, and the line coefficient of thermal expansion was 44.5x10⁻⁶/degree C.

[0067] (10) next, a conductor -- thickness it is thin on the front face of the wrap conductor

layer 10 from a Cu-nickel-P alloy in a circuit 9 and the front face of a filler 5 the 2.5-micrometer roughening layer (concave convex layer) 11 — forming — further — the front face of this roughening layer 11 — thickness 0.3-micrometer Sn layer was formed (not shown about refer to drawing 2 (c) and Sn layer). The formation approach is as follows. Namely, carry out acid cleaning of the substrate, and carry out software etching and, subsequently it processes with the catalyst solution which consists of a palladium chloride and an organic acid. Copper-sulfate 8 g/l, a nickel sulfate after giving Pd catalyst and activating this catalyst 0.6 g/l, citric-acid 15 g/l, sodium hypophosphite 29 g/l, boric-acid 31 g/l, and surfactant 0.1 g/l and the nonelectrolytic plating bath which consists of pH=9 — plating — giving — copper — a conductor — thickness it is thin from a Cu-nickel-P alloy on the surface of a circuit The 2.5-micrometer roughening layer 11 was formed. Furthermore, pH=1.2 which consists of 0.1 mol/l hoe stannous-fluoride-1.0 mol/l thiourea liquid At the temperature of 50 degrees C, it is immersed in a non-electrolyzed tin permutation plating bath for 1 hour, a Cu-Sn substitution reaction is carried out to it, and it is thickness to the front face of said roughening layer. 0.3-micrometer Sn layer was prepared (not shown about Sn layer).

[0068] (11) The adhesives A and B for nonelectrolytic plating were prepared as follows.

A. They are 35 weight sections, the photosensitive monomer (Toagosei make and ARONIKKUSU M315) 3.15 weight section, and a defoaming agent (the Sannopuko make, S-65) about 25% acrylic ghost of the preparation **. cresol novolak mold epoxy resin (the Nippon Kayaku make, molecular weight 2500) of the adhesives for nonelectrolytic plating for the upper layers. The 0.5 weight sections and NMP Stirring mixing of the 3.6 weight sections was carried out.

**. The polyether sulfone (PES) 12 weight section, mean particle diameter of an epoxy resin particle (Mitsuhiro formation make, the polymer pole) 1.0 micrometers The 7.2 weight sections, mean particle diameter After mixing the 3.09 weight sections for a 0.5-micrometer thing, the NMP30 weight section was added further and stirring mixing was carried out with the bead mill.

**. The imidazole curing agent (Shikoku formation make, 2E4 MZ-CN) 2 weight section, the photoinitiator (product made from Kanto chemistry, benzophenone) 2 weight section, and photosensitizer (the product made from the Hodogaya chemistry, and EAB) 0.2 Stirring mixing of the weight section and the NMP 1.5 weight section was carried out. These were mixed and the adhesives for nonelectrolytic plating for the upper layers were obtained.

[0069] B. They are 35 weight sections, the photosensitive monomer (Toagosei make and ARONIKKUSU M315) 4 weight section, and a defoaming agent (the Sannopuko make, S-65) about 25% acrylic ghost of the preparation **. cresol novolak mold epoxy resin (the Nippon Kayaku make, molecular weight 2500) of the adhesives for nonelectrolytic plating for lower layers. The 0.5 weight sections and NMP Stirring mixing of the 3.6 weight sections was carried out.

**. The polyether sulfone (PES) 12 weight section, mean particle diameter of an epoxy resin particle (Mitsuhiro formation make, the polymer pole) 0.5-micrometer thing After mixing the 14.49 weight sections, the NMP30 weight section was added further and stirring mixing was carried out with the bead mill.

**. The imidazole curing agent (Shikoku formation make, 2E4 MZ-CN) 2 weight section, the photoinitiator (Ciba-Geigy make, IRUGA cure I-907) 2 weight section, and photosensitizer (the Nippon Kayaku make, DETX-S) Stirring mixing of the 0.2 weight sections and the NMP 1.5 weight section was carried out. These were mixed and the adhesives for nonelectrolytic plating for lower layers were obtained.

[0070] (12) adhesives B for nonelectrolytic plating (viscosity 1.5 – 3.2 Pa-s) prepared above (11) Adhesives A for nonelectrolytic plating (viscosity 5 – 20 Pa-s) After using and applying the roll coater to both sides of a substrate one by one and leaving it to them for 20 minutes in the level condition, desiccation for 30 minutes was carried out to them at 60 degrees C, and with a thickness of 40 micrometers adhesives layer 12b (two-layer structure) was formed in them (refer to drawing 2 (d)). Furthermore, the polyethylene terephthalate film was stuck through the binder on this adhesives layer 12b.

[0071] (13) Stick the photo-mask film with which the black spot of 85 micrometerphi was printed to both sides of the substrate in which said adhesives layer 12b was formed, and it is an

ultrahigh pressure mercury lamp. 500 mJ/cm² It exposed. By carrying out spray development of this with a DMDG solution, opening used as the Bahia hall of 85 micrometerphi was formed in adhesives layer 12b. Furthermore, it is the substrate concerned with an ultrahigh pressure mercury lamp 3000 mJ/cm² It exposes and is 1 hour and after that at 100 **. By carrying out heat-treatment of 5 hours at 150 degrees C, with a thickness of 35 micrometers adhesives layer (resin insulating layer between layers) 12b which has opening (opening 13 for the Bahia hall formation) excellent in the dimensional accuracy equivalent to a photo-mask film was formed (refer to drawing 2 (e)). In addition, a roughening layer is partially exposed to opening used as the Bahia hall.

[0072] (14) Dissolution removal of the epoxy resin particle which is immersed in a chromic acid for 19 minutes, and exists the substrate in which the opening 13 for the Bahia hall formation was formed in an adhesives layer front face was carried out, and the front face of the adhesives layer concerned was roughened, and after being immersed in the neutralization solution (product made from SHIPUREI) after that, it rinsed.

[0073] (15) The catalyst nucleus was given to the front face of adhesives layer 12b and the opening 13 for the Bahia halls by giving a palladium catalyst (product made from ATOTEKKU) to the substrate which performed the surface roughening process (a roughening depth of 3 micrometers).

[0074] (16) To this substrate, it is the above (1). Non-electrolytic copper plating was performed similarly and the non-electrolytic copper plating film with a thickness of 0.6 micrometers was formed in the whole split face (refer to drawing 3 (a)). At this time, since the plating film was thin, irregularity was observed in the nonelectrolytic plating film front face.

[0075] (17) a commercial photopolymer film (dry film) is stuck on the non-electrolytic copper plating film 14, and a mask is laid -- 100 mJ/cm² it exposes -- the development was carried out by the 0.8% sodium carbonate, and the plating resist 16 with a thickness of 15 micrometers was formed (refer to drawing 3 (b)).

[0076] (18) next, the above (1) the same -- carrying out -- electrolytic copper plating -- giving -- the electrolytic copper plating film 15 with a thickness of 15 micrometers -- forming -- a conductor -- thickness attachment of a circuit part and the Bahia hall part was performed (refer to drawing 3 (c)).

[0077] (19) a conductor with a thickness of 16 micrometers which carries out etching processing of the nonelectrolytic plating film 14 under the plating resist 16 with the mixed liquor of a sulfuric acid and a hydrogen peroxide, carries out dissolution removal and consists of non-electrolytic copper plating film 14 and electrolytic copper plating film 15 after carrying out exfoliation removal of the plating resist 16 by KOH 5% -- the circuit 9 (the Bahia hall 17 is included) was formed (refer to drawing 3 (d)).

[0078] (20) the above (19) -- a conductor -- the substrate in which the circuit 9 (the Bahia hall 17 is included) was formed -- copper-sulfate 8 g/l and nickel sulfate 0.6 g/l, citric-acid 15 g/l, sodium hypophosphite 29 g/l, a 31g [/l.] boric acid, and surfactant the nonelectrolytic plating liquid of pH=9 which consists of 0.1 g/l -- being immersed -- this -- a conductor -- the roughening layer 11 which consists of with a thickness of 3 micrometers copper-nickel-Lynn on the surface of a circuit was formed. When the roughening layer 11 was analyzed by EPMA (X-ray fluorescence) at this time, the presentation ratio of nickel 1.5mol % and P 0.5 mol% was shown Cu 98mol%. And further, the substrate was washed in cold water, it was immersed in the non-electrolyzed tin permutation plating bath which consists of 0.1 mol/l hoe ****-ized tin-1.0 mol/l thiourea liquid at 50 degrees C for 1 hour, and the tin permutation plating layer with a thickness of 0.05 micrometers was formed in the front face of said roughening layer 11 (however, not shown about a tin permutation plating layer).

[0079] (21) repeating the process of aforementioned (12) - (20) -- further -- the upper resin insulating-layer 12between layers b, and a conductor -- the one-layer laminating of the circuit 9 (the Bahia hall 17 is included) was carried out, and the multilayer-interconnection substrate was obtained (refer to drawing 4 (a)). in addition -- here -- a conductor -- although the roughening layer 11 which consists of copper-nickel-Lynn on the surface of a circuit is formed, a tin permutation plating layer is not formed in this roughening layer 11 front face.

[0080] (22) Oligomer of the photosensitive grant which, on the other hand, acrylic-ized 50% of epoxy groups of 60% of the weight of the cresol novolak mold epoxy resin (Nippon Kayaku make) dissolved in DMDG (molecular weight 4000) The 46.67 weight sections, 80% of the weight of the bisphenol A mold epoxy resin (the product made from oil-ized shell --) dissolved in the methyl ethyl ketone the Epicoat 1001 14.121 weight section and an imidazole curing agent (Shikoku -- formation -- make --) the multiple-valued acrylic monomer (the Nippon Kayaku make --) which are the 2E4 MZ-CN1.6 weight section and a photosensitive monomer the R604 1.5 weight section -- the same -- a multiple-valued acrylic monomer (the product made from the Kyoeisha chemistry --) the leveling agent (the Kyoeisha make --) which consists of the DPE6A 3.0 weight section and an acrylic ester polymerization object The poly flow No.75 0.36 weight section is mixed, and it is the IRUGA cure I-907 (Ciba-Geigy make) as a photoinitiator to this mixture. The 2.0 weight sections, DETX-S as a photosensitizer (Nippon Kayaku make) The 0.2 weight sections are added and it is DMDG (diethylene-glycol wood ether)1.0 further. The weight section was added and the solder resist constituent which adjusted viscosity to 1.4×10^{-3} Pa-s at 25 degrees C was obtained. In addition, measurement of viscosity is a Brookfield viscometer (Tokyo Keiki and DVL-B mold). In the case of 60rpm, they are rotor No.4 and 6rpm. The case was based on rotor No.4.

[0081] (23) The above-mentioned solder resist constituent was applied to both sides of the multilayer-interconnection substrate obtained above (21) by the thickness of 20 micrometers. Subsequently, the side in which the chromium layer was formed in the soda lime glass substrate with a thickness of 5mm with which the circle pattern (mask pattern) of solder resist opening was drawn by the chromium layer after performing for 20 minutes at 70 degrees C and performing desiccation processing for 30 minutes at 70 degrees C is stuck in a solder resist layer, and they are 1000 mJ/cm². The DMTG development was exposed and carried out by ultraviolet rays. Furthermore, it heat-treated at 120 degree C by 100 degree C for 1 hour for 1 hour, and heat-treated [80 degrees C] on the conditions of 3 hours by 150 degree C for 1 hour, and the solder resist (diameter of opening 200 micrometers) layer 18 (thickness of 20 micrometers) in which the pad part carried out opening was formed.

[0082] (24) Next, the substrate in which the solder resist layer 18 was formed was immersed in the non-electrolyzed nickel-plating liquid of pH=5 which consists of nickel chloride 30 g/l, sodium hypophosphite 10 g/l, and sodium-citrate 10 g/l for 20 minutes, and the nickel-plating layer 19 with a thickness of 5 micrometers was formed in opening. Furthermore, the substrate was immersed in the non-electrolyzed gilding liquid which consists of gold cyanide potassium 2 g/l, ammonium-chloride 75 g/l, sodium-citrate 50 g/l, and sodium hypophosphite 10 g/l for 23 seconds on 93-degree C conditions, and the gilding layer 20 with a thickness of 0.03 micrometers was formed on the nickel-plating layer 19.

[0083] (25) And print soldering paste to opening of the solder resist layer 18. By carrying out a reflow at 200 degrees C, the solder bump (solder object) 21 was formed and the multilayer printed wiring board which has the solder bump 21 was manufactured (refer to drawing 4 (b)). In addition, tin-silver, a tin-indium, tin-zinc, a tin-bismuth, etc. can be used as solder.

[0084] (Example 1 of a comparison) The multilayer printed wiring board which has a solder bump like an example 1 was manufactured except having made the through hole screen-stencil and harden conductive paste (the Tatsuta Electric Wire & Cable make, DD paste XAE1209).

[0085] Thus, about the multilayer printed wiring board of the manufactured example 1 and the example 1 of a comparison, it is humidity. 100%, temperature On the conditions of 121 degrees C and two atmospheric pressures The PCT (pressure cooker test) trial left for 200 hours was carried out, and the existence [through hole / the Bahia hall and] of an open circuit was checked. Consequently, with the patchboard of the example 1 of a comparison, the open circuit was seen to an open circuit not having been observed between the conductor layer and the through hole in the patchboard of an example 1. When this carries out the cross cut of the patchboard of the example 1 of a comparison in the through hole section and observes it with an optical microscope, conductive paste is carrying out hardening contraction, a clearance occurs between a through hole and the hardening object of the conductive paste, water collects here, and it serves as a gas with heating, pushes up the conductor layer on a through hole, and is

presumed to have attained to the open circuit.

[Translation done.]

*** NOTICES ***

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3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] (a) – (f) It is drawing showing a part of process which manufactures the multilayer printed wiring board of this invention.

[Drawing 2] (a) – (e) It is drawing showing a part of process which manufactures the multilayer printed wiring board of this invention.

[Drawing 3] (a) – (d) It is drawing showing a part of process which manufactures the multilayer printed wiring board of this invention.

[Drawing 4] (a) and (b) It is drawing showing a part of process which manufactures the multilayer printed wiring board of this invention.

[Description of Notations]

- 1 Substrate
- 2 Copper Foil
- 3 Through Hole
- 4 11 Roughening layer
- 5 Filler
- 6 14 Nonelectrolytic plating film
- 7 15 Electrolysis plating film
- 8 Etching Resist
- 9 Conductor — Circuit
- 10 Conductor Layer
- 12a Resin bulking agent
- 12b The resin insulating layer between layers (adhesives layer)
- 13 Opening for Bahia Halls
- 16 Plating Resist
- 17 Bahia Hall
- 18 Solder Resist Layer
- 19 Nickel-Plating Layer
- 20 Gilding Layer
- 21 Solder Bump (Solder Object)

[Translation done.]

*** NOTICES ***

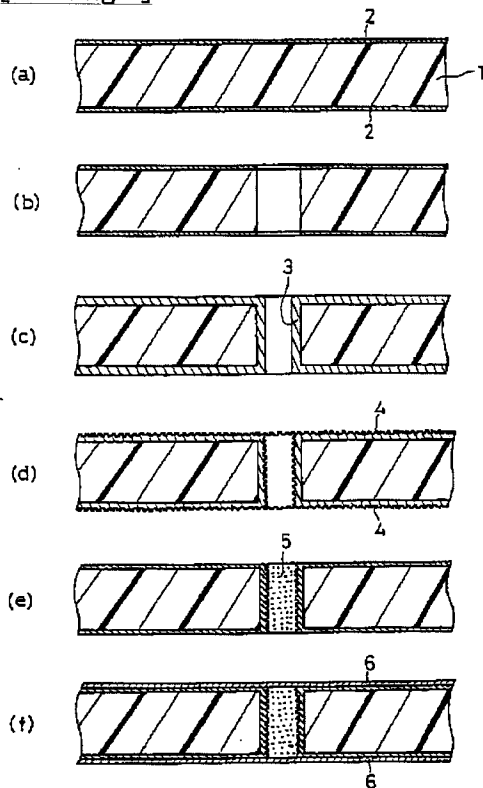
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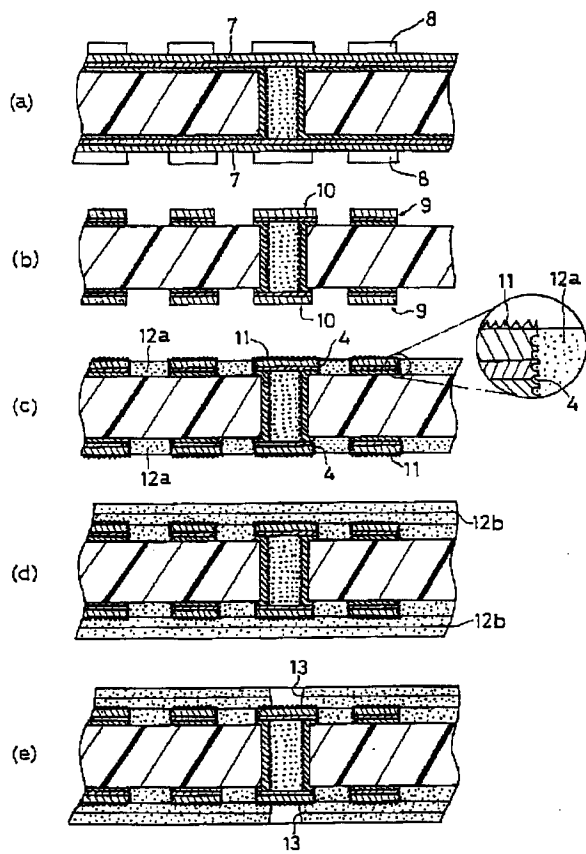
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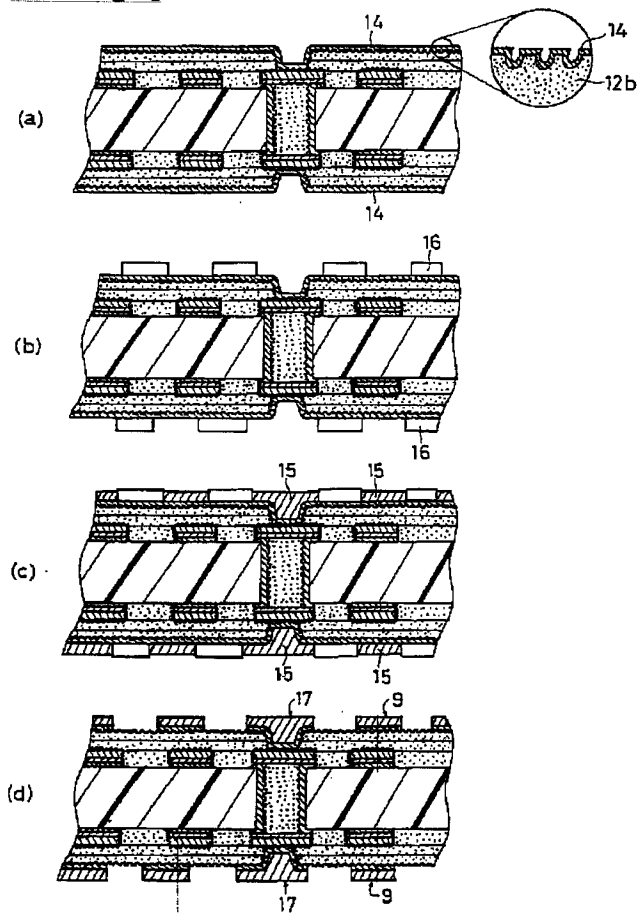
3.In the drawings, any words are not translated.

DRAWINGS

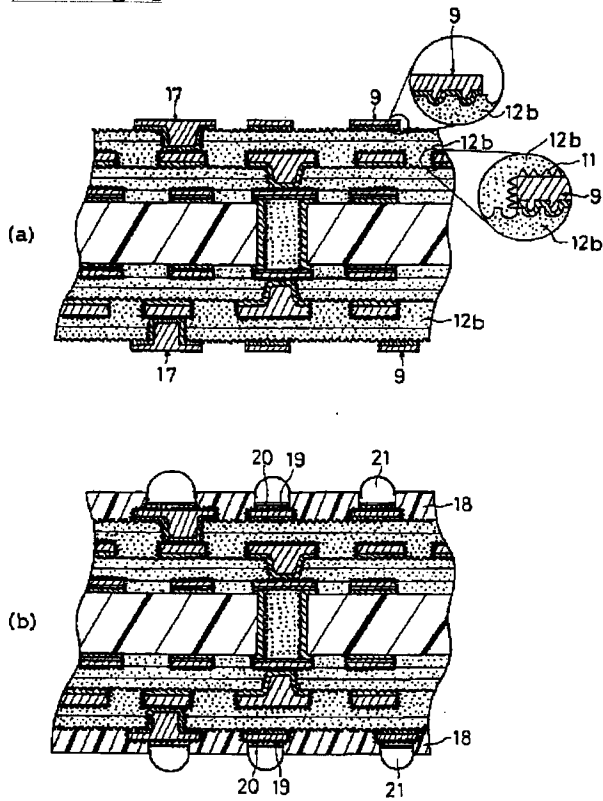
[Drawing 1]**[Drawing 2]**



[Drawing 3]



[Drawing 4]



[Translation done.]

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(54)【発明の名称】 多層プリント配線板

(57)【要約】

【課題】 充填材の硬化収縮を抑制してスルーホールと
パイアホールの接続信頼性を確保したプリント配線板を
提供すること。

【解決手段】 本発明の多層プリント配線板は、導体層
を有する基板上に、層間樹脂絶縁層と導体層を交互に積
層して内外層の導体層どうしをパイアホールにて接続し
たビルドアップ配線層が形成されている多層プリント配
線板において、前記基板には、表面および裏面を電氣的
に接続するスルーホールが形成され、そのスルーホール
には金属粒子を含む非導電性の充填材が充填され、さら
にその充填材のスルーホールからの露出面を覆う導体層
が形成されていることを特徴とする。

【特許請求の範囲】

【請求項1】 導体層を有する基板上に、層間樹脂絶縁層と導体層を交互に積層して内外層の導体層どうしをバイアホールにて接続したビルドアップ配線層が形成されている多層プリント配線板において、

前記基板には、表面および裏面を電氣的に接続するスルーホールが形成され、そのスルーホールには金属粒子を含む非導電性の充填材が充填され、さらにその充填材のスルーホールからの露出面を覆う導体層が形成されていることを特徴とする多層プリント配線板。

【請求項2】 充填材を覆う前記導体層にはバイアホールが接続されていることを特徴とする請求項1に記載の多層プリント配線板。

【請求項3】 前記充填材は、金属粒子、樹脂および無機超微粉末からなることを特徴とする請求項1または2に記載の多層プリント配線板。

【請求項4】 前記充填材は、比抵抗が $1\text{ M}\Omega\cdot\text{cm}$ 以上であることを特徴とする請求項1～3のいずれか1に記載の多層プリント配線板。

【請求項5】 前記金属粒子は、平均粒径が $0.1\sim 30\mu\text{m}$ であることを特徴とする請求項1～4のいずれか1に記載の多層プリント配線板。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、多層プリント配線板に関し、特に、充填材の硬化収縮を抑制してスルーホールとバイアホールの接続信頼性を確保した多層プリント配線板について提案する。

【0002】

【従来の技術】近年、ICチップを実装するパッケージ基板は、電子工業の進歩に伴う電子機器の小型化あるいは高速化に対応し、ファインパターンによる高密度化および信頼性の高いものが求められている。

【0003】このようなパッケージ基板として、例えば、特開平5-243728号公報には、めっきスルーホールに導電ペーストを充填し、この導電ペーストを被覆する導体層を形成したものが開示されている。

【0004】

【発明が解決しようとする課題】ところが、上掲の従来技術に係るパッケージ基板では、導電ペーストを使用しているため、樹脂を硬化収縮させて導電性を生じさせる必要があった。このため、かかるパッケージ基板では、充填材の硬化収縮に起因した隙間が導電ペーストとスルーホール内壁の導体との間に生じやすく、高温、多湿条件下に曝すと、導電ペーストを被覆する導体層が剥離したり、スルーホールとバイアホールと間で断線が発生するといった問題が生じた。

【0005】そこで、本発明は、充填材の硬化収縮を抑制してスルーホールとバイアホールの接続信頼性を確保したプリント配線板を提供することを目的とする。

【0006】

【課題を解決するための手段】発明者らは、上記目的の実現に向け鋭意研究した結果、下記内容を要旨構成とする発明に想到した。

(1) 本発明の多層プリント配線板は、導体層を有する基板上に、層間樹脂絶縁層と導体層を交互に積層して内外層の導体層どうしをバイアホールにて接続したビルドアップ配線層が形成されている多層プリント配線板において、前記基板には、表面および裏面を電氣的に接続するスルーホールが形成され、そのスルーホールには金属粒子を含む非導電性の充填材が充填され、さらにその充填材のスルーホールからの露出面を覆う導体層が形成されていることを特徴とする。

【0007】なお、上記多層プリント配線板において、充填材を覆う前記導体層にはバイアホールが接続されていることが好ましく、前記充填材は、金属粒子、樹脂および平均粒径が好ましくは $1\sim 1000\text{nm}$ の無機超微粉末からなることが好ましい。また、前記充填材は、比抵抗が $1\text{ M}\Omega\cdot\text{cm}$ 以上、より望ましくは $1\times 10^8\Omega\cdot\text{cm}$ 以上であり、前記金属粒子は、その平均粒径が $0.1\sim 30\mu\text{m}$ であることが好ましい。

【0008】

【発明の実施の形態】このような本発明の多層プリント配線板は、スルーホールを埋める材料として金属粒子を含む充填材を使用しているため、充填材とその充填材を覆う導体層との密着性に優れ、また非導電性の充填材を使用しているため、金属粒子を含む充填材に導電性をもたせるための硬化収縮を付与する必要がなく、スルーホール内壁導体からの充填材の剥離を防止することができる。このような剥離が存在すると、高温多湿条件下では水が溜り、この水が揮発する際に導体層を押し上げて剥離させてしまうからである。

【0009】特に本発明では、充填材として、金属粒子、樹脂、および平均粒径が好ましくは $1\sim 1000\text{nm}$ （より好ましくは $2\sim 100\text{nm}$ ）の無機超微粉末からなる組成物を用いることが望ましい。この理由は、無機超微粉末の分子間力によって形成される網目状構造が金属粒子をトラップし、その金属粒子は沈降することがない。このため、充填材表面に金属粒子が突出し、この金属粒子とそれを被覆する導体層が一体化してその密着性を向上させることができるからである。これにより、充填材とスルーホール導体層との剥離を防止し、高温多湿条件下でも充填材とこの充填材を被覆する導体層との剥離が発生しなくなる。

【0010】ここで、前記充填材を構成する金属粒子としては、銅、金、銀、アルミニウム、ニッケル、チタン、クロム、すず／鉛、パラジウムなどが使用できる。この金属粒子は、樹脂との密着性を改善するために、その表面に錯化剤などの金属表面改質剤などを付与してもよい。この金属粒子は、その平均粒径が $0.1\sim 30\mu\text{m}$ で

あることが好ましい。この理由は、充填材を被覆する導体層との密着性を確保できる範囲だからである。また、この金属粒子の配合量は、充填材の全固形分に対して30～90重量%とすることが望ましい。この理由は、密着性および印刷性を同時に確保できる範囲だからである。

【0011】また、前記充填材を構成するマトリックス樹脂としては、熱硬化性樹脂、熱可塑性樹脂を用いることができる。熱硬化性樹脂としては、エポキシ樹脂、ポリイミド樹脂、フェノール樹脂から選ばれるいずれか少なくとも1種の樹脂がよい。熱可塑性樹脂としては、ポリテトラフルオロエチレン(PTFE)、4フッ化エチレン6フッ化プロピレン共重合体(FEP)、4フッ化エチレンパーフロロアルコキシ共重合体(PFA)等のフッ素樹脂、ポリエチレンテレフタレート(PET)、ポリスルホン(PSF)、ポリフェニレンスルフィド(PPS)、熱可塑性ポリフェニレンエーテル(PPE)、ポリエーテルスルホン(PES)、ポリエーテルイミド(PEI)、ポリフェニレンスルホン(PPEs)、ポリエチレンナフタレート(PEN)、ポリエーテルエーテルケトン(PEEK)、ポリオレフィン系樹脂から選ばれるいずれか少なくとも1種がよい。

【0012】特に、充填材に用いられる最適樹脂としては、ビスフェノール型エポキシ樹脂およびノボラック型エポキシ樹脂から選ばれるいずれか少なくとも1種がよい。この理由は、ビスフェノール型エポキシ樹脂は、A型、F型などの樹脂を適宜選択することにより、希釈溶媒を使用しなくてもその粘度を調整でき、またノボラック型エポキシ樹脂は、高強度で耐熱性や耐薬品性に優れ、無電解めっき液のような強塩基性溶液中でも分解せず、また熱分解しないからである。前記ビスフェノール型エポキシ樹脂としては、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂から選ばれるいずれか少なくとも1種を用いることが望ましい。なかでも、ビスフェノールF型エポキシ樹脂は、低粘度で無溶剤で使用することができるため有利である。前記ノボラック型エポキシ樹脂としては、フェノールノボラック型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂から選ばれるいずれか少なくとも1種を用いることが望ましい。このような樹脂の中で、ノボラック型エポキシ樹脂とビスフェノール型エポキシ樹脂を配合して用いる場合、その配合割合は、重量比で1/1～1/100が望ましい。この理由は、粘度の上昇を抑制しつつ、金属粒子の沈降を防止できる範囲だからである。

【0013】前記充填材を構成する無機超微粒子としては、シリカ、アルミナ、炭化珪素、ムライトを用いることが望ましい。なかでもシリカが最適である。この無機超微粒子の平均粒径は、1～1000nm、より好ましくは2～100nmとする。この理由は、粒子径が微細であるため、スルーホール内の充填性を損なうことなく、また水素結合と推定される結合を網目状に形成でき、粒子状物質

をトラップできる範囲だからである。この無機超微粉末の配合量は、充填材の全固形分に対して0.1～5重量%とすることが望ましい。この理由は、充填性を損なうことなく、硬化収縮を防止できる範囲だからである。

【0014】なお、このような樹脂組成物に使用される硬化剤としては、イミダゾール系硬化剤、酸無水物硬化剤、アミン系硬化剤が望ましい。硬化収縮が小さいからである。硬化収縮を抑制することにより、充填材とそれを被覆する導体層との一体化してその密着性を向上させることができる。

【0015】また、このような硬化前の樹脂組成物は、必要に応じて溶剤で希釈することができる。この溶剤としては、NMP(ノルマルメチルピロリドン)、DMDG(ジエチレングリコールジメチルエーテル)、グリセリン、水、1-又は2-又は3-のシクロヘキサノール、シクロヘキサノン、メチルセルソルブ、メチルセルソルブアセテート、メタノール、エタノール、ブタノール、プロパノールなどがある。

【0016】本発明では、充填材の比抵抗を、 $10^6 \Omega \cdot \text{cm}$ 以上、より好ましくは $10^8 \Omega \cdot \text{cm}$ 以上とし、非導電性とする。この理由は、充填材を導電性になると、その樹脂組成物を硬化したのち研磨する際に、研磨くずが導体回路間に付着し、ショートの原因となるからである。また、上記樹脂組成物は、導電性を付与するには硬化収縮させる必要があるが、硬化収縮させることは充填材を被覆する導体層との剥離を招くことになるので好ましくないからである。

【0017】本発明では、スルーホールおよび充填材を覆う導体層上にパイアホールが接続されていてもよい。この理由は、スルーホールによるデッドスペースを無くすることができるからである。

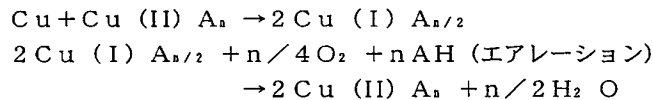
【0018】本発明では、配線密度を高くするために、基板の内層に導体層が形成されていることが望ましい。このとき、基板は、導体層とプリプレグを交互に積層して形成されてなる。例えば、基板は、ガラス繊維やアラミド繊維の布あるいは不織布に樹脂を含浸させてBステージとしたプリプレグを、銅箔や回路基板と交互に積層し、加熱プレスして一体化することにより形成される。

【0019】本発明では、充填材が充填されるスルーホール内の内壁導体表面に粗化層が形成されていることが望ましい。この理由は、充填材とスルーホールとが粗化層を介して密着し隙間が発生しないからである。もし、充填材とスルーホールとの間に空隙が存在すると、その直上に電解めっきで形成される導体層は、平坦なものとならなかったり、空隙中の空気が熱膨張してクラックや剥離を引き起こしたりし、また一方で、空隙に水が溜まってマイグレーションやクラックの原因となったりする。この点、粗化層が形成されているとこのような不良発生を防止することができる。

【0020】また、本発明において、充填材を覆う導体

層の表面には、スルーホール内壁の導体表面に形成した粗化層と同様の粗化層が形成されていることが有利である。この理由は、粗化層により層間樹脂絶縁層やパイアホールとの密着性を改善することができるからである。特に、導体層の側面に粗化層が形成されていると、導体層側面と層間樹脂絶縁層との密着不足によってこれらの界面を起点として層間樹脂絶縁層に向けて発生するクラックを抑制することができる。

【0021】このようなスルーホール内壁や導体層の表面に形成される粗化層の厚さは、0.1~10 μ mがよい。この理由は、厚すぎると層間ショートの原因となり、薄すぎると被着体との密着力が低くなるからである。この粗化層としては、スルーホール内壁の導体あるいは導体*



Aは錯化剤（キレート剤として作用）、nは配位数である。

【0024】この処理で用いられる第二銅錯体は、アゾール類の第二銅錯体がよい。このアゾール類の第二銅錯体は、金属銅などを酸化するための酸化剤として作用する。アゾール類としては、ジアゾール、トリアゾール、テトラゾールがよい。なかでもイミダゾール、2-メチルイミダゾール、2-エチルイミダゾール、2-エチル-4-メチルイミダゾール、2-フェニルイミダゾール、2-ウンデシルイミダゾールなどがよい。このアゾール類の第二銅錯体の含有量は、1~15重量%がよい。この範囲内にあれば、溶解性および安定性に優れるからである。

【0025】また、有機酸は、酸化銅を溶解させるために配合させるものである。具体例としては、ギ酸、酢酸、プロピオン酸、酪酸、吉草酸、カブロン酸、アクリル酸、クロトン酸、シュウ酸、マロン酸、コハク酸、グルタル酸、マレイン酸、安息香酸、グリコール酸、乳酸、リンゴ酸、スルファミン酸から選ばれるいずれか少なくとも1種がよい。この有機酸の含有量は、0.1~30重量%がよい。酸化された銅の溶解性を維持し、かつ溶解安定性を確保するためである。なお、発生した第一銅錯体は、酸の作用で溶解し、酸素と結合して第二銅錯体となって、再び銅の酸化に寄与する。また、有機酸に加えて、ホウフッ酸、塩酸、硫酸などの無機酸を添加してもよい。

【0026】この有機酸-第二銅錯体からなるエッチング液には、銅の溶解やアゾール類の酸化作用を補助するために、ハロゲンイオン、例えば、フッ素イオン、塩素イオン、臭素イオンなどを加えてもよい。このハロゲンイオンは、塩酸、塩化ナトリウムなどを添加して供給できる。ハロゲンイオン量は、0.01~20重量%がよい。この範囲内にあれば、形成された粗化層は層間樹脂絶縁層との密着性に優れるからである。

*層の表面を、酸化（黒化）-還元処理して形成したもの、有機酸と第二銅錯体の混合水溶液で処理して形成したもの、あるいは銅-ニッケル-リン針状合金のめっき処理にて形成したものがよい。

【0022】これらの処理のうち、酸化（黒化）-還元処理による方法では、NaOH (20g/l)、NaClO₂ (50g/l)、Na₃PO₄ (15.0g/l)を酸化浴（黒化浴）、NaOH (2.7g/l)、NaBH₄ (1.0g/l)を還元浴とする。

【0023】また、有機酸-第二銅錯体の水溶液を用いた処理では、スプレーやバブリングなどの酸素共存条件下で次のように作用し、導体回路である銅などの金属箔を溶解させる。

【0027】この有機酸-第二銅錯体からなるエッチング液は、アゾール類の第二銅錯体および有機酸（必要に応じてハロゲンイオン）を、水に溶解して調製する。

【0028】また、銅-ニッケル-リンからなる針状合金のめっき処理では、硫酸銅1~40g/l、硫酸ニッケル0.1~6.0g/l、クエン酸10~20g/l、次亜リン酸塩10~100g/l、ホウ酸10~40g/l、界面活性剤0.01~10g/lからなる液組成のめっき浴を用いることが望ましい。

【0029】本発明において、ビルドアップ配線層で使用される層間樹脂絶縁層としては、熱硬化性樹脂、熱可塑性樹脂、あるいは熱硬化性樹脂と熱可塑性樹脂の複合体を用いることができる。熱硬化性樹脂としては、エポキシ樹脂、ポリイミド樹脂、フェノール樹脂、熱硬化性ポリフェニレンエーテル（PPE）などが使用できる。熱可塑性樹脂としては、ポリテトラフルオロエチレン（PTFE）、4フッ化エチレン6フッ化プロピレン共重合体（FEP）、4フッ化エチレンパーフロロアルコキシ共重合体（PFA）等のフッ素樹脂、ポリエチレンテレフタレート（PET）、ポリスルホン（PSF）、ポリフェニレンスルフィド（PPS）、熱可塑性ポリフェニレンエーテル（PPE）、ポリエーテルスルホン（PES）、ポリエーテルイミド（PEI）、ポリフェニレンスルホン（PPES）、ポリエチレンナフタレート（PEN）、ポリエーテルエーテルケトン（PEEK）、ポリオレフィン系樹脂などを使用できる。熱硬化性樹脂と熱可塑性樹脂の複合体としては、エポキシ樹脂-PES、エポキシ樹脂-PSF、エポキシ樹脂-PPS、エポキシ樹脂-PPESなどが使用できる。

【0030】本発明では、層間樹脂絶縁層としてガラスクロス含浸樹脂複合体を用いることができる。このガラスクロス含浸樹脂複合体としては、ガラスクロス含浸エポキシ、ガラスクロス含浸ビスマレイミドトリアジン、

ガラスクロス含浸PTFE、ガラスクロス含浸PPE、ガラスクロス含浸ポリイミドなどがある。

【0031】また本発明において、層間樹脂絶縁層としては、無電解めっき用接着剤を用いることができる。この無電解めっき用接着剤としては、硬化処理された酸あるいは酸化剤に可溶性の耐熱性樹脂粒子が、硬化処理によって酸あるいは酸化剤に難溶性となる未硬化の耐熱性樹脂中に分散されてなるものが最適である。この理由は、酸や酸化剤で処理することにより、耐熱性樹脂粒子が溶解除去されて、表面に蛸つば状のアンカーからなる粗化面を形成できるからである。粗化面の深さは、0.01~20 μ mがよい。密着性を確保するためである。また、セミアディティブプロセスにおいては、0.1~5 μ mがよい。密着性を確保しつつ、無電解めっき膜を除去できる範囲だからである。

【0032】上記無電解めっき用接着剤において、特に硬化処理された前記耐熱性樹脂粒子としては、①平均粒径が10 μ m以下の耐熱性樹脂粉末、②平均粒径が2 μ m以下の耐熱性樹脂粉末を凝集させた凝集粒子、③平均粒径が2~10 μ mの耐熱性樹脂粉末と平均粒径が2 μ m以下の耐熱性樹脂粉末との混合物、④平均粒径が2~10 μ mの耐熱性樹脂粉末の表面に平均粒径が2 μ m以下の耐熱性樹脂粉末または無機粉末のいずれか少なくとも1種を付着させてなる疑似粒子、⑤平均粒径が0.1~0.8 μ mの耐熱性樹脂粉末と平均粒径が0.8 μ mを超え2 μ m未満の耐熱性樹脂粉末との混合物、⑥平均粒径が0.1~1.0 μ mの耐熱性樹脂粉末、から選ばれるいずれか少なくとも1種を用いることが望ましい。これらは、より複雑なアンカーを形成できるからである。この無電解めっき用接着剤で使用する耐熱性樹脂は、前述の熱硬化性樹脂、熱可塑性樹脂、熱硬化性樹脂と熱可塑性樹脂の複合体を使用できる。

【0033】本発明において、基板上に形成された導体層（スルーホールに充填された充填材を覆うものを含む）と層間樹脂絶縁層上に形成された導体回路は、パイアホールで接続することができる。この場合、パイアホールは、めっき膜や導電ペーストで充填されたものがよい。

【0034】次に、本発明の多層プリント配線板を製造する方法について一例を挙げて具体的に説明する。なお、以下に述べる方法は、セミアディティブ法による多層プリント配線板の製造方法に関するものであるが、本発明における多層プリント配線板の製造方法では、フルアディティブ法やマルチラミネーション法、ピンラミネーション法を採用することができる。

【0035】(1) まず、基板にドリルで貫通孔を明け、貫通孔の内壁面を含む基板表面に無電解めっきを施してスルーホールを形成する。基板としては、ガラスエポキシ基板やポリイミド基板、ビスマレイミドトリアジン樹脂基板、フッ素樹脂基板などの樹脂基板、あるいはこ

れらの樹脂の銅張積層板、セラミック基板、金属基板などを用いることができる。特に、誘電率を考慮する場合は、両面銅張フッ素樹脂（ポリテトラフルオロエチレン等）基板を用いることが好ましい。この基板は、片面が粗化された銅箔をフッ素樹脂基板に熱圧着したものである。無電解めっきとしては銅めっきがよい。フッ素樹脂基板のようにめっきのつきまわりが悪い基板の場合は、有機酸などからなる前処理液（商品名：テトラエッチ）を用いた処理、プラズマ処理などの表面改質を行う。

【0036】(2) 次に、厚付けのために電解めっきを行う。この電解めっきとしては銅めっきがよい。そしてさらに、スルーホール内壁および電解めっき膜表面を粗化処理して粗化層を設けてもよい。この粗化層には、酸化（黒化）-還元処理によるもの、有機酸と第二銅錯体の混合水溶液をスプレー処理（エッチング処理）して形成したもの、あるいは銅-ニッケル-リン針状合金めっきによるものがある。

【0037】これらの処理のなかで、無電解めっきにより粗化層を形成する場合は、銅イオン濃度、ニッケルイオン濃度、次亜リン酸イオン濃度が、それぞれ $2.2 \times 10^{-2} \sim 4.1 \times 10^{-2}$ mol/l、 $2.2 \times 10^{-3} \sim 4.1 \times 10^{-3}$ mol/l、0.20~0.25 mol/l である組成のめっき水溶液を用いることが望ましい。この範囲で析出する被膜の結晶構造は針状構造になり、アンカー効果に優れるからである。この無電解めっき水溶液には、上記化合物に加えて錯化剤や添加剤を加えてもよい。また、0.01~10 g/l の界面活性剤を加えてもよい。この界面活性剤としては、例えば、日信化学工業製のサーフィノール440、465、485 などのアセチレン含有ポリオキシエチレン系界面活性剤を用いることが望ましい。即ち、無電解めっきにより粗化層を形成する場合は、硫酸銅 1~40 g/l、硫酸ニッケル 0.1~6.0 g/l、クエン酸 10~20 g/l、次亜リン酸塩 10~100 g/l、ホウ酸 10~40 g/l、界面活性剤 0.01~10 g/l からなる液組成のめっき水溶液を用いることが望ましい。

【0038】酸化還元処理により粗化層を形成する場合は、NaOH (20 g/l)、NaClO₂ (50 g/l)、Na₃PO₄ (15.0 g/l) を酸化浴とし、NaOH (2.7 g/l)、NaBH₄ (1.0 g/l) を還元浴とすることが望ましい。

【0039】有機酸と第二銅錯体の混合水溶液を用いるエッチング処理により粗化層を形成する場合は、メック（株）製のCZ8100液に代表されるが、液中に含まれる2価の銅の酸化力を利用して銅表面を凹凸にする。

【0040】粗化層は、イオン化傾向が銅より大きくチタン以下である金属あるいは貴金属の層で被覆されていてもよい。この理由は、前記金属あるいは貴金属の層は、粗化層を被覆し、層間絶縁層を粗化処理する際に導体回路の局部電極反応を防止してその導体回路の溶解を防止するからである。この層の厚さは0.01~2 μ mがよい。このような金属としては、チタン、アルミニウム、

亜鉛、鉄、インジウム、タリウム、コバルト、ニッケル、スズ、鉛、ビスマスから選ばれる少なくとも1種がある。また、貴金属としては、金、銀、白金、パラジウムがある。なかでも、スズは、無電解置換めっきにより薄い層を形成でき、粗化層に追従できるため有利である。このスズの場合は、ホウフッ化スズ-チオ尿素、塩化スズ-チオ尿素液を使用し、Cu-Snの置換反応により0.01~2 μ m程度のSn層が形成される。一方、貴金属の場合は、スパッタや蒸着などの方法が採用される。

【0041】(3) 次に、スルーホール内に、前述した構成の充填材を充填する。具体的には、充填材は、スルーホール部分に開口を設けたマスクを載置した基板上に、印刷法にて塗布することによりスルーホール内に充填され、充填後、乾燥、硬化される。硬化条件としては、50~160℃で0.5~5時間であることが望ましい。

【0042】さらに、スルーホールからはみ出した充填材および基板の電解めっき膜表面の粗化層を研磨により除去して、基板表面を平坦化する。この研磨は、ベルトサンダーやバフ研磨がよい。この研磨により、金属粒子の一部が表面に露出し、この露出した部分の金属粒子と導体層のめっき皮膜が一体化して、良好な密着性が発現する。

【0043】(4) 前記(3)で平坦化した基板の表面に触媒核を付与した後、無電解めっきを施し、厚さ0.1~5 μ m程度の無電解めっき膜を形成し、さらに必要に応じて電解めっきを施し、厚さ5~25 μ mの電解めっき膜を設ける。次に、めっき膜の表面に、感光性のドライフィルムを加熱プレスによりラミネートし、パターンが描画されたフォトマスクフィルム（ガラス製がよい）を載置し、露光した後、現像液で現像してエッチングレジストを設ける。そして、エッチングレジスト非形成部分の導体をエッチング液で溶解除去することにより、導体回路部分および充填材を覆う導体層部分を形成する。そのエッチング液としては、硫酸-過酸化水素の水溶液、過硫酸アンモニウムや過硫酸ナトリウム、過硫酸カリウムなどの過硫酸塩水溶液、塩化第二鉄や塩化第二銅の水溶液がよい。

【0044】(5) そして、エッチングレジストを剥離して、独立した導体回路および導体層とした後、その導体回路および導体層の表面に、粗化層を形成する。導体回路および充填材を覆う導体層の表面に粗化層を形成すると、その導体は、層間樹脂絶縁層との密着性に優れるので、導体回路および充填材を覆う導体層の側面と樹脂絶縁層との界面を起点とするクラックが発生しない。また一方で、充填材を覆う導体層は、電気的に接続されるパイアホールとの密着性が改善される。この粗化層の形成方法は、前述したとおりであり、酸化（黒化）-還元処理、針状合金めっき、あるいはエッチングして形成する方法などがある。さらに、粗化後に、導体回路間に樹脂を充填し、表面を研磨して平滑化してもよい。この場

合、研磨後に、導体回路表面を粗化することが望ましい。このときの充填樹脂としては、ビスフェノールF型エポキシ樹脂、イミダゾール硬化剤および平均粒子径0.1~30 μ mの無機粒子からなる組成物がよい。

【0045】(6) このようにして作製した配線基板の上に、層間樹脂絶縁層を形成する。層間樹脂絶縁層としては、熱硬化性樹脂、熱可塑性樹脂、あるいは熱硬化性樹脂と熱可塑性樹脂の複合体を使用できる。また、本発明では、層間樹脂絶縁材として前述した無電解めっき用接着剤を用いることができる。層間樹脂絶縁層は、これらの樹脂の未硬化液をロールコートやカーテンコートなどを用いて塗布したり、フィルム状の樹脂を熱圧着してラミネートすることにより形成される。なお、この状態では、導体回路パターン上の層間樹脂絶縁層の厚さが薄く、大面積を持つ導体回路上の層間樹脂絶縁層の厚さが厚くなり凹凸が発生していることが多いため、金属板や金属ロールを用い、加熱しながら押圧して、層間樹脂絶縁層の表面を平坦化することが望ましい。

【0046】(7) 次に、この層間樹脂絶縁層に被覆される下層の導体回路（スルーホール）との電気的接続を確保するために層間樹脂絶縁層に開口を設ける。この開口の穿孔は、層間樹脂絶縁層が感光性樹脂からなる場合は、露光、現像処理にて行い、熱硬化性樹脂や熱可塑性樹脂からなる場合は、レーザー光にて行う。このとき、使用されるレーザー光としては、炭酸ガスレーザー、紫外線レーザー、エキシマレーザーなどがある。レーザー光にて孔明けした場合は、デスミア処理を行ってもよい。このデスミア処理は、クロム酸、過マンガン酸塩などの水溶液からなる酸化剤を使用して行うことができ、また酸素プラズマ、酸素およびCF₄の混合ガスプラズマなどで処理してもよい。

【0047】(8) 開口を形成した層間樹脂絶縁層の表面を必要に応じて粗化する。上述した無電解めっき用接着剤を層間樹脂絶縁層として使用した場合は、その絶縁層の表面を酸や酸化剤で処理して耐熱性樹脂粒子のみを選択的に溶解または分解除去して粗化する。酸としては、リン酸、塩酸、硫酸、あるいは蟻酸や酢酸などの有機酸があるが、特に有機酸を用いることが望ましい。粗化処理した場合に、パイアホールから露出する金属導体層を腐食させにくいからである。酸化剤としては、クロム酸、過マンガン酸塩（過マンガン酸カリウムなど）を用いることが望ましい。また、熱硬化性樹脂や熱可塑性樹脂を使用した場合でも、クロム酸、過マンガン酸塩などの水溶液から選ばれる酸化剤による表面粗化処理が有効である。なお、酸化剤では粗化されないフッ素樹脂（ポリテトラフルオロエチレン等）などの樹脂の場合は、プラズマ処理やテトラエッチ（潤工社製の金属ナフタレン化合物）などにより表面を粗化する。

【0048】(9) 次に、前記層間樹脂絶縁層の粗化面に無電解めっき用の触媒核を付与する。一般に触媒核は、

パラジウムスズコロイドであり、この溶液に基板を浸漬、乾燥、加熱処理して樹脂表面に触媒核を固定する。また、金属核をCVD、スパッタ、プラズマにより樹脂表面に打ち込んで触媒核とすることができる。この場合、樹脂表面に金属核が埋め込まれることになり、この金属核を中心にめっきが析出して導体回路が形成されるため、粗化しにくい樹脂やフッ素樹脂（ポリテトラフルオロエチレン等）のように樹脂と導体回路との密着が悪い樹脂でも、密着性を確保できる。この金属核としては、パラジウム、銀、金、白金、チタン、銅およびニッケルから選ばれるいずれか少なくとも1種以上がよい。なお、金属核の量は、 $20\mu\text{g}/\text{cm}^2$ 以下がよい。この量を超えると金属核を除去しなければならないからである。

【0049】(10)次に、層間樹脂絶縁層の粗化面に無電解めっきを施し、全面に無電解めっき膜を形成する。この無電解めっき膜の厚みは $0.1\sim 5\mu\text{m}$ 、より望ましくは $0.5\sim 3\mu\text{m}$ である。無電解めっきは、無電解銅めっきがよい。そのめっき液としては、常法のものを使用でき、例えば、 $29\text{g}/\text{l}$ の硫酸銅、 $25\text{g}/\text{l}$ の炭酸ナトリウム、 $140\text{g}/\text{l}$ の酒石酸塩、 $40\text{g}/\text{l}$ の水酸化ナトリウム、 37% ホルムアルデヒド 150ml 、 $\text{pH}=11.5$ からなる組成のものがよい。

【0050】(11)前記(10)で形成した無電解めっき膜上に、めっきレジストを形成する。めっきレジストは、前述のように、感光性樹脂フィルム（ドライフィルム）をラミネートし、露光、現像処理することにより形成される。

【0051】(12)さらに、めっきレジスト非形成部分に電解めっきを施し、導体回路部分（バイアホール部分を含む）を厚付けする。ここで、上記電解めっきとしては、銅めっきを用いることが望ましく、その厚みは、 $5\sim 30\mu\text{m}$ がよい。また、前記バイアホール内には、電解めっき膜を充填していわゆるフィルドピアを形成することが望ましい。この理由は、層間樹脂絶縁層の平坦性を*

〔電解めっき水溶液〕

硫酸 $180\text{g}/\text{l}$

硫酸銅 $80\text{g}/\text{l}$

添加剤（アトテックジャパン製、商品名：カバラシドGL）

$1\text{ml}/\text{l}$

〔電解めっき条件〕

電流密度 $1\text{A}/\text{dm}^2$

時間 30分

温度 室温

【0056】(2) 全面に無電解銅めっき膜と電解銅めっき膜からなる導体（スルーホールを含む）を形成した基板を、水洗いし、乾燥した後、 NaOH ($20\text{g}/\text{l}$)、 NaClO_2 ($50\text{g}/\text{l}$)、 Na_3PO_4 ($15.0\text{g}/\text{l}$) を酸化浴（黒化浴）、 NaOH ($2.7\text{g}/\text{l}$)、 NaBH_4 ($1.0\text{g}/\text{l}$) を還元浴とする酸化還元処理に供し、そのスルーホール3を

*確保できるからである。さらに、前記バイアホールは、基板に設けたスルーホールの直上に形成されていてもよい。高密度化のためである。

【0052】(13)めっきレジストを剥離した後、そのめっきレジスト下の無電解めっき膜を、硫酸と過酸化水素の混合水溶液、過硫酸ナトリウムや過硫酸アンモニウムや過硫酸ナトリウム、過硫酸カリウムなどの過硫酸塩水溶液、塩化第二鉄や塩化第二銅の水溶液などのエッチング液で溶解除去し、独立した導体回路（バイアホールを含む）とする。さらに、露出した粗化面上のパラジウム触媒核をクロム酸などで溶解除去する。

【0053】(14)そして、この基板上に前述の工程を繰り返してさらに上層の導体回路を設けることができる。以下、実施例をもとに説明する。

【0054】

〔実施例〕（実施例1）

(1) 厚さ 0.8mm のBT（ビスマレイミドトリアジン）樹脂基板1に片面粗化された $18\mu\text{m}$ の銅箔2がラミネートされている銅張積層板を出発材料とした（図1(a)参照）。まず、この銅張積層板をドリル削孔し（図1(b)参照）、ついでパラジウムスズコロイドを付着させ、下記組成および条件にて無電解めっきを施した。

〔無電解めっき水溶液〕

EDTA $150\text{g}/\text{l}$

硫酸銅 $20\text{g}/\text{l}$

HCHO $30\text{ml}/\text{l}$

NaOH $40\text{g}/\text{l}$

α 、 α' -ピピリジル $80\text{mg}/\text{l}$

PEG $0.1\text{g}/\text{l}$

〔無電解めっき条件〕

70°C の液温度で30分

【0055】ついで、以下の条件で電解銅めっきを施し、厚さ $15\mu\text{m}$ の電解銅めっき膜を形成した（図1(c)参照）。

含む導体の全表面に粗化層4を設けた（図1(d)参照）。

【0057】〔スルーホール用充填材の調製〕クレゾールノボラック型エポキシ樹脂（油化シェル製、エピコート152）3.5重量部、ビスフェノールF型エポキシ樹脂（油化シェル製、エピコート807）14.1重量部、平均粒子径 14nm のシリカ超微粉末（アエロジルR202）1.0重量部を3本ローラにて混練し、さらに、イミダゾール硬化剤（四国化成製、2E4MZ-CN）1.2重量部、平均粒子径 $15\mu\text{m}$ の銅粉100重量部を加えて3本ローラにて混練

し、これらの混合物の粘度を $22 \pm 1^\circ\text{C}$ で $200 \sim 1000 \text{ Pa} \cdot \text{s}$ に調整して、スルーホール用充填材5を調製した。

【0058】(3) 調製した充填材5を、スルーホール3内にスクリーン印刷によって充填し、乾燥した後、 80°C 、 100°C でそれぞれ1時間づつ、さらに 150°C で1時間の加熱により硬化させた。そして、導体上面の粗化面およびスルーホール3からはみ出した充填材5を、#400のベルト研磨紙(三共理化学製)を用いたベルトサンダー研磨により除去し、さらに、このベルトサンダー研磨による傷を取り除くために、アルミナ砥粒やSiC砥粒によるパフ研磨を行い、基板表面を平坦化した(図1(e)参照)。

【0059】(4) 前記(3)で平坦化した基板表面に、パラジウム触媒(アトテック製)を付与し、前記(1)と同じ条件で無電解銅めっきを施すことにより、厚さ $0.6 \mu\text{m}$ の無電解銅めっき膜6を形成した(図1(f)参照)。

【0060】(5) ついで、前記(1)と同じ条件で電解銅めっきを施し、厚さ $15 \mu\text{m}$ の電解銅めっき膜7を形成し、導体回路9となる部分の厚付け、およびスルーホール3に充填された充填材5を覆う導体層(円形のスルーホールランド)10となる部分を形成した。

【0061】(6) 導体回路9および導体層10となる部分を形成した基板の両面に、市販の感光性ドライフィルムを張りつけ、マスクを載置して、 $100 \text{ mJ}/\text{cm}^2$ で露光、 0.8% 炭酸ナトリウム水溶液で現像処理し、厚さ $15 \mu\text{m}$ のエッチングレジスト8を形成した(図2(a)参照)。

【0062】(7) エッチングレジスト8を形成していない部分のめっき膜を、硫酸と過酸化水素の混合液を用いるエッチング液で溶解除去して、さらにエッチングレジスト8を $5\% \text{ KOH}$ で剥離除去して、独立した導体回路9および充填材5を覆う導体層10を形成した(図2(b)参照)。さらに、酸化還元処理して側面を含む導体表面を前記(2)と同様にして粗化処理した。

【0063】〔樹脂充填剤の調製〕

①. ビスフェノールF型エポキシモノマー(油化シェル製、分子量310, YL983U) 100重量部、表面にシランカップリング剤がコーティングされた平均粒径 $1.6 \mu\text{m}$ で SiO_2 球状粒子(アドマテック製、CRS 1101-CE、ここで、最大粒子の大きさは後述する内層銅パターンの厚み($15 \mu\text{m}$)以下とする) 170重量部、レベリング剤(サンノプロ製、ベレノールS4) 1.5重量部を3本ロールにて混練して、その混合物の粘度を $23 \pm 1^\circ\text{C}$ で $45,000 \sim 49,000 \text{ cps}$ に調整した。

②. イミダゾール硬化剤(四国化成製、2E4MZ-CN) 6.5重量部。これらを混合して樹脂充填剤12aを調製した。

【0064】(8) 調製した樹脂充填剤12aを、基板の片面にスクリーン印刷にて塗布することにより、導体回路9または導体層10の間に充填し、 70°C 、20分間で乾燥させ、他方の面についても同様にして樹脂充填剤12aを導体回路9または導体層10の間に充填し、 70°C 、20分間で

乾燥させた。即ち、この工程により、樹脂充填剤12aが内層銅パターン間に充填される。

【0065】(9) 前記(8)の処理を終えた基板の片面を、#400のベルト研磨紙(三共理化学製)を用いたベルトサンダー研磨により、内層銅パターン9、10の表面に樹脂充填剤12aが残らないように研磨し、次いで、前記ベルトサンダー研磨による傷を取り除くためのパフ研磨を行った。このような一連の研磨を基板の他方の面についても同様に行った。次いで、 100°C で1時間、 120°C で3時間、 150°C で1時間、 180°C で7時間の加熱処理を行って樹脂充填剤12aを硬化した。

【0066】このようにして、導体回路9または導体層10の間に充填された樹脂充填剤12aの表層部および導体回路9または導体層10上面の粗化層11を除去して基板両面を平滑化し、樹脂充填剤12aと導体回路9または導体層10の側面とが粗化層11を介して強固に密着した基板を得た。即ち、この工程により、樹脂充填剤12aの表面と内層銅パターンの表面が同一平面となる。ここで、充填した硬化樹脂のTg点は 155.6°C 、線熱膨張係数は $44.5 \times 10^{-6}/^\circ\text{C}$ であった。

【0067】(10)次に、導体回路9および充填材5の表面を覆う導体層10の表面にCu-Ni-P合金からなる厚さ $2.5 \mu\text{m}$ の粗化層(凹凸層)11を形成し、さらにこの粗化層11の表面に厚さ $0.3 \mu\text{m}$ のSn層を形成した(図2(c)参照、Sn層については図示しない)。その形成方法は以下のものである。即ち、基板を酸性脱脂してソフトエッチングし、次いで、塩化パラジウムと有機酸からなる触媒溶液で処理して、Pd触媒を付与し、この触媒を活性化した後、硫酸銅 $8 \text{ g}/\text{l}$ 、硫酸ニッケル $0.6 \text{ g}/\text{l}$ 、クエン酸 $15 \text{ g}/\text{l}$ 、次亜リン酸ナトリウム $29 \text{ g}/\text{l}$ 、ホウ酸 $31 \text{ g}/\text{l}$ 、界面活性剤 $0.1 \text{ g}/\text{l}$ 、 $\text{pH}=9$ からなる無電解めっき浴にてめっきを施し、銅導体回路の表面にCu-Ni-P合金からなる厚さ $2.5 \mu\text{m}$ の粗化層11を形成した。さらに、 $0.1 \text{ mol}/\text{l}$ ホウフッ化スズ $1.0 \text{ mol}/\text{l}$ チオ尿素液からなる $\text{pH}=1.2$ の無電解スズ置換めっき浴に、温度 50°C で1時間浸漬してCu-Sn置換反応させ、前記粗化層の表面に厚さ $0.3 \mu\text{m}$ のSn層を設けた(Sn層については図示しない)。

【0068】(11)無電解めっき用接着剤A、Bを次のように調製した。

A. 上層用の無電解めっき用接着剤の調製

①. クレゾールノボラック型エポキシ樹脂(日本化薬製、分子量2500)の25%アクリル化物を35重量部、感光性モノマー(東亜合成製、アロニックスM315) 3.15重量部、消泡剤(サンノプロ製、S-65) 0.5重量部、NMPを3.6重量部を攪拌混合した。

②. ポリエーテルスルホン(PES) 12重量部、エポキシ樹脂粒子(三洋化成製、ポリマーボール)の平均粒径 $1.0 \mu\text{m}$ を7.2重量部、平均粒径 $0.5 \mu\text{m}$ のものを3.09重量部、を混合した後、さらにNMP 30重量部を添加

し、ビーズミルで攪拌混合した。

③. イミダゾール硬化剤（四国化成製、2E4MZ-CN）2重量部、光開始剤（関東化学製、ベンゾフェノン）2重量部、光増感剤（保土ヶ谷化学製、EAB）0.2重量部、NMP 1.5重量部を攪拌混合した。これらを混合して上層用の無電解めっき用接着剤を得た。

【0069】B. 下層用の無電解めっき用接着剤の調製

①. クレゾールノボラック型エポキシ樹脂（日本化薬製、分子量2500）の25%アクリル化物を35重量部、感光性モノマー（東亜合成製、アロニックスM315）4重量部、消泡剤（サンノプロ製、S-65）0.5重量部、NMPを3.6重量部を攪拌混合した。

②. ポリエーテルスルホン（PES）12重量部、エポキシ樹脂粒子（三洋化成製、ポリマーボール）の平均粒径 $0.5\mu\text{m}$ のものを14.49重量部、を混合した後、さらにNMP 30重量部を添加し、ビーズミルで攪拌混合した。

③. イミダゾール硬化剤（四国化成製、2E4MZ-CN）2重量部、光開始剤（チバガイギー製、イルガキュア I-907）2重量部、光増感剤（日本化薬製、DET-X-S）0.2重量部、NMP 1.5重量部を攪拌混合した。これらを混合して下層用の無電解めっき用接着剤を得た。

【0070】(12)前記(11)で調製した無電解めっき用接着剤B（粘度 $1.5\sim 3.2\text{ Pa}\cdot\text{s}$ ）と無電解めっき用接着剤A（粘度 $5\sim 20\text{ Pa}\cdot\text{s}$ ）を、基板の両面に、順次ロールコートを用いて塗布し、水平状態で20分間放置してから、 60°C で30分間の乾燥を行い、厚さ $40\mu\text{m}$ の接着剤層12b（2層構造）を形成した（図2(d)参照）。さらに、この接着剤層12b上に粘着剤を介してポリエチレンテレフタレートフィルムを貼付した。

【0071】(13)前記接着剤層12bを形成した基板の両面に、 $85\mu\text{m}$ φの黒円が印刷されたフォトマスクフィルムを密着させ、超高圧水銀灯により $500\text{mJ}/\text{cm}^2$ で露光した。これをDMDG溶液でスプレー現像することにより、接着剤層12bに $85\mu\text{m}$ φのバイアホールとなる開口を形成した。さらに、当該基板を超高圧水銀灯にて $3000\text{mJ}/\text{cm}^2$ で露光し、 100°C で1時間、その後 150°C で5時間の加熱処理をすることにより、フォトマスクフィルムに相当する寸法精度に優れた開口（バイアホール形成用開口13）を有する厚さ $35\mu\text{m}$ の接着剤層（層間樹脂絶縁層）12bを形成した（図2(e)参照）。なお、バイアホールとなる開口には、粗化層を部分的に露出させる。

【0072】(14)バイアホール形成用開口13を形成した基板を、クロム酸に19分間浸漬し、接着剤層表面に存在するエポキシ樹脂粒子を溶解除去して、当該接着剤層の表面を粗化し、その後、中和溶液（シブレイ社製）に浸漬してから水洗した。

【0073】(15)粗面化処理（粗化深さ $3\mu\text{m}$ ）を行った基板に対し、パラジウム触媒（アトテック製）を付与することにより、接着剤層12bおよびバイアホール用開

口13の表面に触媒核を付与した。

【0074】(16)この基板に、前記(1)と同様にして無電解銅めっきを施し、粗面全体に厚さ $0.6\mu\text{m}$ の無電解銅めっき膜を形成した（図3(a)参照）。このとき、めっき膜が薄いため無電解めっき膜表面には凹凸が観察された。

【0075】(17)市販の感光性樹脂フィルム（ドライフィルム）を無電解銅めっき膜14に張り付け、マスクを載置して、 $100\text{mJ}/\text{cm}^2$ で露光し、0.8%炭酸ナトリウムで現像処理し、厚さ $15\mu\text{m}$ のめっきレジスト16を設けた（図3(b)参照）。

【0076】(18)次に、前記(1)と同様にして電解銅めっきを施し、厚さ $15\mu\text{m}$ の電解銅めっき膜15を形成し、導体回路部分およびバイアホール部分の厚付けを行った（図3(c)参照）。

【0077】(19)めっきレジスト16を5%KOHで剥離除去した後、そのめっきレジスト16下の無電解めっき膜14を硫酸と過酸化水素の混合液でエッチング処理して溶解除去し、無電解銅めっき膜14と電解銅めっき膜15からなる厚さ $16\mu\text{m}$ の導体回路9（バイアホール17を含む）を形成した（図3(d)参照）。

【0078】(20)前記(19)で導体回路9（バイアホール17を含む）を形成した基板を、硫酸銅 $8\text{g}/\text{l}$ 、硫酸ニッケル $0.6\text{g}/\text{l}$ 、クエン酸 $15\text{g}/\text{l}$ 、次亜リン酸ナトリウム $29\text{g}/\text{l}$ 、ホウ酸 $31\text{g}/\text{l}$ 、界面活性剤 $0.1\text{g}/\text{l}$ からなる $\text{pH}=9$ の無電解めっき液に浸漬し、該導体回路の表面に厚さ $3\mu\text{m}$ の銅-ニッケル-リンからなる粗化層11を形成した。このとき、粗化層11をEPMA（蛍光X線分析）で分析したところ、Cu 98mol%、Ni 1.5mol%、P 0.5mol%の組成比を示した。そしてさらに、その基板を水洗いし、 $0.1\text{mol}/\text{l}$ ホウふっ化スズ- $1.0\text{mol}/\text{l}$ チオ尿素液からなる無電解スズ置換めっき浴に 50°C で1時間浸漬し、前記粗化層11の表面に厚さ $0.05\mu\text{m}$ のスズ置換めっき層を形成した（但し、スズ置換めっき層については図示しない）。

【0079】(21)前記(12)～(20)の工程を繰り返すことにより、さらに上層の層間樹脂絶縁層12bと導体回路9（バイアホール17を含む）を1層積層し、多層配線基板を得た（図4(a)参照）。なお、ここでは、導体回路の表面に銅-ニッケル-リンからなる粗化層11を設けるが、この粗化層11表面にはスズ置換めっき層を形成しない。

【0080】(22)一方、DMDGに溶解させた60重量%のクレゾールノボラック型エポキシ樹脂（日本化薬製）のエポキシ基50%をアクリル化した感光性付与のオリゴマー（分子量4000）を46.67重量部、メチルエチルケトンに溶解させた80重量%のビスフェノールA型エポキシ樹脂（油化シェル製、エピコート1001）14.121重量部、イミダゾール硬化剤（四国化成製、2E4MZ-CN）1.6重量部、感光性モノマーである多価アクリルモノマー（日本

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化薬製、R604) 1.5 重量部、同じく多価アクリルモノマー (共栄社化学製、DPE6A) 3.0 重量部、アクリル酸エステル重合体からなるレベリング剤 (共栄社製、ポリフローNo.75) 0.36 重量部を混合し、この混合物に対して光開始剤としてのイルガキュア I-907 (チバガイギー製) 2.0 重量部、光増感剤としての DETX-S (日本化薬製) 0.2 重量部を加え、さらに DMDG (ジエチレングリコールジメチルエーテル) 1.0 重量部を加えて、粘度を 25℃ で $1.4 \pm 0.3 \text{ Pa} \cdot \text{s}$ に調整したソルダーレジスト組成物を得た。なお、粘度測定は、B 型粘度計 (東京計器、DVL-B 型) で 60rpm の場合はローター No.4、6 rpm の場合はローター No.4 によった。

【0081】(23) 前記(21)で得られた多層配線基板の両面に、上記ソルダーレジスト組成物を $20 \mu\text{m}$ の厚さで塗布した。次いで、70℃ で 20 分間、70℃ で 30 分間の乾燥処理を行った後、クロム層によってソルダーレジスト開口部の円パターン (マスクパターン) が描画された厚さ 5 mm のソーダライムガラス基板を、クロム層が形成された側をソルダーレジスト層に密着させて $1000 \text{ mJ}/\text{cm}^2$ の紫外線で露光し、DMTG 現象処理した。さらに、80℃ で 1 時間、100℃ で 1 時間、120℃ で 1 時間、150℃ で 3 時間の条件で加熱処理し、パッド部分が開口した (開口径 $200 \mu\text{m}$) ソルダーレジスト層 18 (厚み $20 \mu\text{m}$) を形成した。

【0082】(24) 次に、ソルダーレジスト層 18 を形成した基板を、塩化ニッケル $30 \text{ g}/\text{l}$ 、次亜リン酸ナトリウム $10 \text{ g}/\text{l}$ 、クエン酸ナトリウム $10 \text{ g}/\text{l}$ からなる $\text{pH} = 5$ の無電解ニッケルめっき液に 20 分間浸漬して、開口部に厚さ $5 \mu\text{m}$ のニッケルめっき層 19 を形成した。さらに、その基板を、シアン化金カリウム $2 \text{ g}/\text{l}$ 、塩化アンモニウム $75 \text{ g}/\text{l}$ 、クエン酸ナトリウム $50 \text{ g}/\text{l}$ 、次亜リン酸ナトリウム $10 \text{ g}/\text{l}$ からなる無電解金めっき液に 93℃ の条件で 23 秒間浸漬して、ニッケルめっき層 19 上に厚さ $0.03 \mu\text{m}$ の金めっき層 20 を形成した。

【0083】(25) そして、ソルダーレジスト層 18 の開口部に、はんだペーストを印刷して 200℃ でリフローすることによりはんだバンプ (はんだ体) 21 を形成し、はんだバンプ 21 を有する多層プリント配線板を製造した (図 4(b) 参照)。なお、はんだとしては、スズ-銀、スズ-インジウム、スズ-亜鉛、スズ-ビスマスなどが使用できる。

【0084】(比較例 1) スルーホールに導電ペースト (タツタ電線製、DD ペースト XAE1209) をスクリーン印刷して硬化させたこと以外は、実施例 1 と同様にしてはんだバンプを有する多層プリント配線板を製造した。

【0085】このようにして製造した実施例 1 と比較例

1 の多層プリント配線板について、湿度 100%、温度 121℃、2 気圧の条件で 200 時間放置する PCT (プレッシャーコッカーテスト) 試験を実施し、バイアホールとスルーホールとの断線の有無を確認した。その結果、実施例 1 の配線板では、導体層とスルーホールとの間で断線が観察されなかったのに対し、比較例 1 の配線板では、その断線が見られた。これは、比較例 1 の配線板をスルーホール部でクロスカットして光学顕微鏡で観察したところ、導電ペーストが硬化収縮しており、スルーホールとその導電ペーストの硬化体との間に隙間が発生し、ここに水が溜まって、加熱により気体となってスルーホール上の導体層を押し上げ、断線に及んだと推定される。

【0086】

【発明の効果】以上説明したように本発明によれば、充填材の硬化収縮を抑制してスルーホールとバイアホールの接続信頼性を確保したプリント配線板を提供することができる。

【図面の簡単な説明】

【図 1】(a)~(f) は、本発明の多層プリント配線板を製造する工程の一部を示す図である。

【図 2】(a)~(e) は、本発明の多層プリント配線板を製造する工程の一部を示す図である。

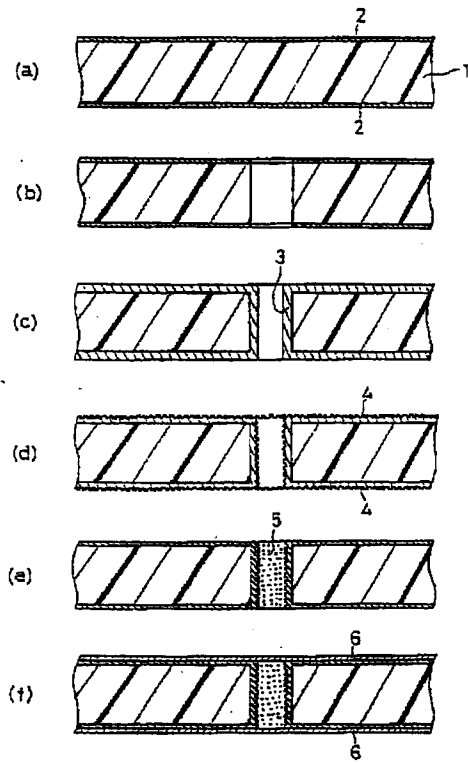
【図 3】(a)~(d) は、本発明の多層プリント配線板を製造する工程の一部を示す図である。

【図 4】(a), (b) は、本発明の多層プリント配線板を製造する工程の一部を示す図である。

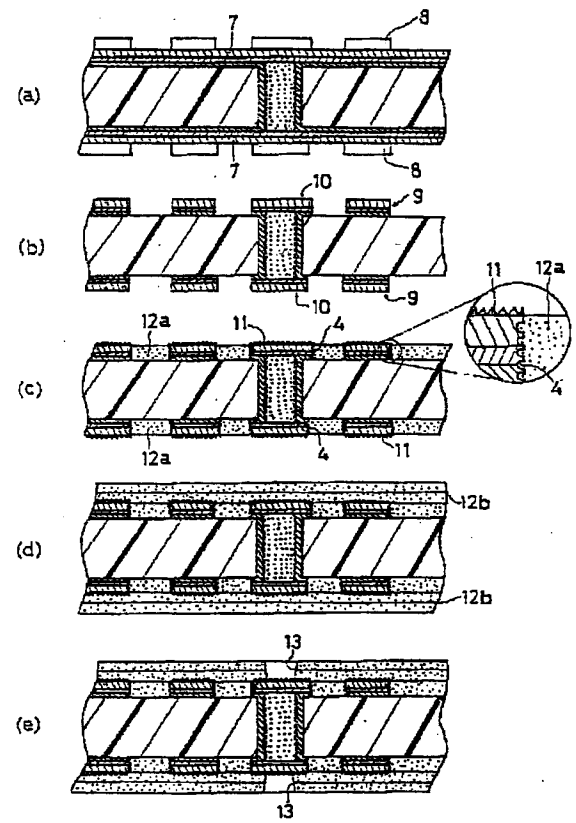
【符号の説明】

- 1 基板
- 2 銅箔
- 3 スルーホール
- 4, 11 粗化層
- 5 充填材
- 6, 14 無電解めっき膜
- 7, 15 電解めっき膜
- 8 エッチングレジスト
- 9 導体回路
- 10 導体層
- 12a 樹脂充填剤
- 12b 層間樹脂絶縁層 (接着剤層)
- 13 バイアホール用開口
- 16 めっきレジスト
- 17 バイアホール
- 18 ソルダーレジスト層
- 19 ニッケルめっき層
- 20 金めっき層
- 21 はんだバンプ (はんだ体)

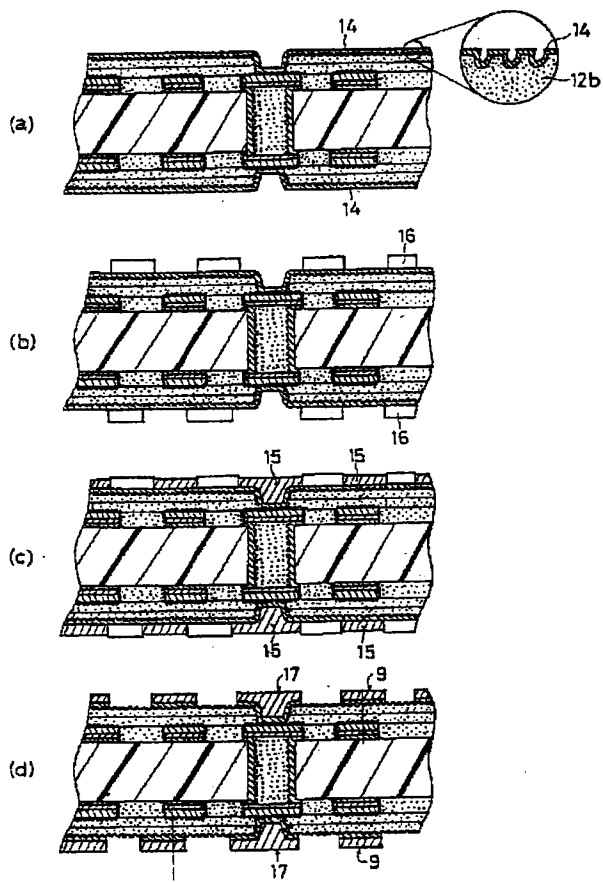
【図 1】



【図 2】



【図 3】



【図 4】

